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IN THIS ISSUE

The Effect of Strain on the Electrical Resistance of Keratin. *J. E. Algie* 1

The Absorption of Dyes by Cellulose Acetate from Nonaqueous Media. *Calvin Heit, Mary Moncrieff-Yeates, Ann Palm, Mildred Stevens, and Howard J. White, Jr.* 6

Comparison of the Mechanical Properties of Cotton Yarns and Fabrics Treated with Anhydrous Ethylamine and with Mercerizing Caustic. *Hilda M. Züfle, F. V. Eggerton, and Leon Segal* 13

Polyamine Resins for Finishing of Hydrophobic Fibers. *Emery I. Valko and Giuliana C. Tesoro* 21

High Strength Regenerated Cellulose Fibers. *D. K. Smith* .. 32

National Cotton Council
Chemical Finishing Conference

Amine Odor in Resin-Treated Fabrics. *A. C. Nuessle, E. O. J. Heiges, and R. A. Olney* 41

Epoxy Resin Blended Finishes for White Cottons. *D. D. Gagliardi and F. B. Shippee* 54

Effect of Creaseproofing Agents on Lightfastness of Sensitive Dyes. *Herman B. Goldstein and David N. Koenig* 66

Recent Developments in Cotton Finishing with Acetal Reactants. *J. B. Irvine, T. J. Cronin, and J. H. Davids* 74

Chlorine Retention in Resin-Treated Cottons. *Hugh H. Mosher* 88

LETTERS TO THE EDITOR

Moisture Regain of Tightly Woven Cotton Fabrics. *E. L. Skau and E. Honold* 96

Book Reviews 98

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TEXTILE RESEARCH JOURNAL

The Effect of Strain on the Electrical Resistance of Keratin

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Abstract

The change of resistance with time after the application of various strains has been examined at 90% RH and 20° C. for keratin fibers. There is an initial instantaneous rise of resistance much greater than that due to a dimensional change, which is related to the strain, followed by a decrease in the resistance caused by the uptake of water vapor from the surrounding atmosphere. A further stage was observed during which the resistance rose as excess water vapor left the fiber.

Introduction

Several workers have examined the effect of mechanical strains and stresses on the resistance or resistivity of fibers. Evershed [1] noticed in cotton a change in the ratio of the resistance at 10 volts to the resistance at 100 volts with increase in pressure of electrodes; Murphy and Walker [7] found no appreciable change in the resistivity of cotton and silk with small changes in tension; Marsh and Earp [6] in an attempt to investigate the capillary theory of conduction made an examination of strain-resistivity and found that *wool* fibers which had been steamed while under a tension of 30 kg./cm.^{2} had an increase of resistivity up to three times that of an untreated fiber or of a fiber steamed without tension; New [8] agrees with the results obtained by Marsh and Earp; Hearle [4] found a small increase in resistivity with increase in tension for cotton but a decrease for viscose. Recently Shigeo Ogawa and Hiroshi Tsuboi [10] have found a change in the resistance of viscose fibers with a change in the draw ratio.

If the mechanical properties of a wool fiber are closely related to the long chain nature of the keratin molecule, it is pertinent to examine changes in the conductivity with mechanical stress and strain with the possibility of determining new information about the molecular organization of electrical conduction in wool fibers.

This paper presents data obtained in a series of experiments on the change of resistance with strain, with particular attention to the time-dependence of the strain/resistivity relationship. An attempt has been made to explain the mechanisms involved. Since the mechanical properties of the keratin fibers are vitally concerned in the strain/resistivity relationships, stress relaxation/time experiments similar to those of Rigby [11] were made in order to determine the mechanical state of the fiber at any time during an experiment.

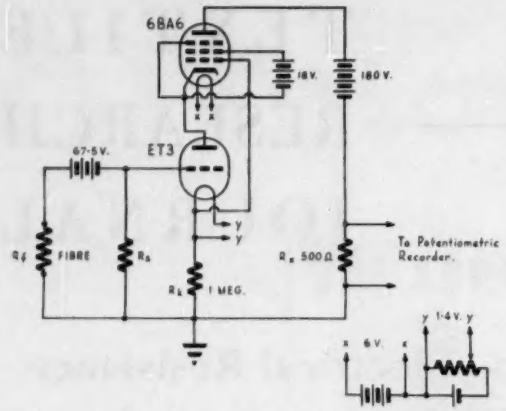

Fig. 1. Electrometer circuit diagram.

Apparatus

Circuit

All measurements of resistance were made using the circuit shown in Figure 1. This circuit is essentially that of a Baldwin-Farmer electrometer [2]; ET3 is an electrometer triode connected as a cathode follower with a 6BA6 pentode to maintain a constant 6V supply between anode and cathode of the ET3. All high voltages are supplies by dry batteries, while accumulators are used for the filament supplies. R_K is a 1-megohm standard resistor, and the current flowing in the electrometer circuit develops a voltage across R_X which is fed to a potentiometric recorder with a sensitivity variable between 1 mV and 50 mV full scale deflection.

R_S is a standard resistor which is regularly compared against other standard resistors. All insulators were covered with a thin layer of silicone grease.

The electrical equipment gave little trouble—dry batteries lasted six months and standard resistors remained constant in comparison with one another. The 6BA6 valve had to be replaced at six-month intervals, probably due to a change of contact potential, which affects its grid base and hence the anode-to-cathode voltage of the ET3 triode.

Good linearity between input and output of the electrometer was obtained beyond 10 volts on the grid of the ET3 triode to ground, provided that the 6BA6 pentode was good. A quick check on this was the anode current of the ET3 with its grid earthed. As the 6BA6 valve changed, the anode current of the ET3 became higher than usual.

With the 67.5-volt dry battery in the circuit as indicated, the stray capacity at the grid of the ET3 was 35 pf, which gave a time constant of 35 sec. in conjunction with a value of $R_s = 10^{12}$ ohms, which was the one generally used. This battery could have been placed on the earth side of the fiber; however, the mechanical design was simpler with the battery in the position shown.

Conditioning Box

The single fiber was held between miniature clamps in a box (Figure 2) which had provision for extending the fiber and which was part of a circulating air system with relative humidity controlled by a sulfuric acid solution [12] at 90% RH or alternately by a saturated solution of potassium chromate giving 88% RH [9] to test whether conditioning by sulfuric acid has any effect on resistance not noticed with salt solutions. The rate of air flow could be controlled. The complete apparatus was contained in a room which had its temperature controlled at 20° ± 0.5° C. Since the room was large, temperature variations were very slow and did not materially affect the experimental results.

The brass fiber clamps and the straining mechanism are shown in Figure 2. The straining screw had 40 threads/in., and by using a dial with 100 graduations the distance between the fiber clamps could be adjusted to within 0.00025 in., provided that a small backlash was avoided. Due to the rigid mounting of the straining mechanism, reproducible adjustment of the straining screw could be obtained.

Experimental Procedure

Single fibers of horsehair or pen-grown Corriedale wool, 0.5–2 cm. long, were used in the experiments. Fibers were selected for uniformity of diameter by microscopic measurements in distilled water. All fibers were cleaned by several changes of cold sulfuric ether, ethyl alcohol, and many changes of distilled water. Each experiment was commenced by first placing a single fiber in the clamps and then setting up the clamps in the conditioning box. Dry air (passing over concentrated H_2SO_4) was passed over the fiber for 1 hr. to ensure that the fiber always started conditioning from the same regain. The conditioning atmosphere was then changed to 90% RH. At least three days of conditioning were found to be necessary to obtain equilibrium regain as determined from the continuous record of resistance with time. Other workers, e.g., Marsh and Earp [6] and Hersh and Montgomery [5], have found it necessary to provide a conditioning time of this duration.

When a stable value of resistance had been obtained, the fiber was extended at a rate of strain of approximately 150%/min. by manually turning the extension screw. A continuous record of resistance changes was obtained during the straining period and for the subsequent period of 1 hr., during which the fiber strain was held constant.

The fiber was then released to the original length between the clamps, and the clamps and fiber were removed from the conditioning box and placed in distilled water at 54° C. for 2 hr. in order to remove residual stresses and to enable the fiber to return to its original length. This process was necessary, as the one fiber was used in a series of experiments in which different strains were applied. The original distance between the clamps was maintained, and the same conditioning procedure was carried out in each experiment. The whole experimental procedure was satisfactory, as it was possible to repeat an experiment on the same fiber and obtain almost identical results.

No difference was observed between results obtained with H_2SO_4 solutions as against those obtained with salt solution. Temperature fluctuations during an experiment were never greater than 0.02° C. and did not have a great effect, since the RH above H_2SO_4 varies little with temperature change [12].

Various air velocities were used in different experiments, but the only effect noticed was a very small change in the later part of the curves in horsehair from 30 min. onwards. It was therefore assumed that it was easy to obtain isothermal conditions with a single fiber. Temperature changes in the fiber due to the mechanical strain also appeared Corriedale fibers at 90% RH and 19.5° C. using the heat conductivity of keratin gave a figure in the millisecond region for the time of heat dissipation. In several of the strain/resistance experiments the fibers were covered with a thin layer of silicone grease about 200μ thick. This lowered the rate of diffusion of water vapor into the fiber by about a decade. It allowed a test to be made of the effect of a change in the rate of entry of water vapor. The silicone grease did not affect the resistance of the fiber, indicating that surface conduction is very small for keratin fibers.

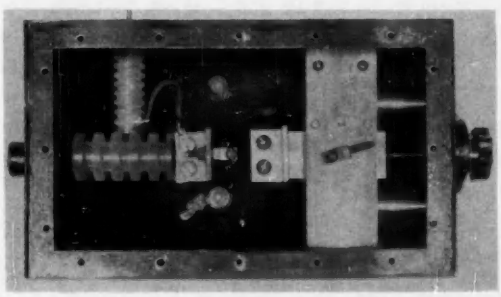

Fig. 2. Photograph of the conditioning box.

Mechanical Experiments

In order that we know the mechanical state of the fibers at any stage of an experiment, stress–relaxation experiments were conducted on horsehair and Corriedale fibers at 90% RH and 19.5° C. using the same strains and rate of straining employed in the resistance vs. strain experiments. Some tests were made on a silicone-covered fiber; this gave the same results as an uncovered fiber, indicating no observable effect of extra water on stress–relaxation.

The time constant of the recording apparatus used in the stress–relaxation experiments was 2 sec. for the horsehair apparatus and 1 msec. for the high-speed recording method used for the Corriedale fiber. Conditioning time was 24 hr. at 90% RH, and the fibers were dried before conditioning commenced.

Results

Figure 3 shows the percentage change in resistance of a single horsehair on the application of strains of 1%, 2%, 5%, 10%, 15%, and 20%. The rate of straining was 150%/min. The temperature in all

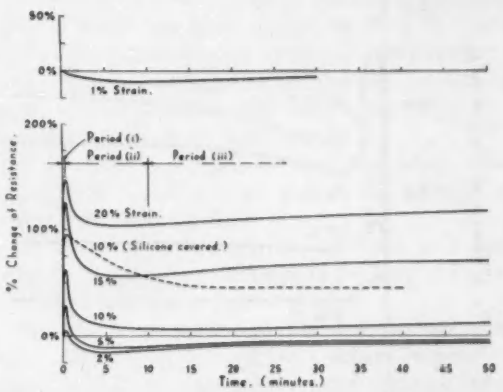

Fig. 3. (Bottom) The change of resistance with time for horsehair after the application of various strains at 90% RH, 19.6° C. (Top) The change of resistance with time for horsehair after the application of 1% strain at 90% RH, 19.6° C.

experiments was 19.6° C. ± 0.02° C., and the RH was 90%. Figure 4 shows similar information for a single Corriedale fiber, for strains of 5%, 10%, 15%, and 20%. The effects of different rates of straining are indicated in Figure 5.

The broken line of Figure 3 is obtained from an experiment on a fiber covered with a 200μ layer of silicone grease. The results of experiments on the relaxation of stress, after a certain strain has been applied, are shown in Figure 7 for pen-grown Corriedale wool fibers and in Figure 6 for horsehair.

Discussion of Results

The results shown in Figures 3–5 may be analyzed by dividing the time scale into three periods:

1. The period during which the fiber is being extended.
2. The period from the end of extending to the point of lowest resistance.
3. The last period, constituting all that occurs after the end of the second period.

During the first period the resistance rises rapidly to a value which increases with the strain. Its maximum value is much greater than could be expected from a change in the dimensions of the fiber, assuming constant fiber volume and constant resistivity. Figure 3 (bottom) shows that a strain of 10% produces a 60% change in resistance, whereas dimensional changes alone would give a 20% change. Also, the maximum value is less than it would be if no water were allowed to enter the fiber during this first period, as can be seen for the case in Figure 3 (bottom) of a fiber covered with silicone grease. An extreme instance is that of the 1% strain in Figure 3 (top), in which the rise of resistance due to extension and the fall of resistance due to water uptake balance each other for 7 sec. after the commencement of extension. The 1% strain graph hence shows no increase of resistance in the first period.

In the second period there is a fall of resistance which appears to be due to the uptake of water vapor by the fiber from the surrounding atmosphere. The fall of resistance takes place at a rate which would be expected from results obtained in microscopic experiments on the time required for different fibers to reach equilibrium swelling when taken from an atmosphere of 60% RH to distilled water. Equilibrium was reached in approximately 1 min. for Corriedale fibers and 15 min. for horsehair. Further evidence in favor of water vapor diffusion into the fiber as an explanation of the fall of resistance in the second period comes from the results obtained for a fiber covered with silicone grease, Figure 3a. This fiber, which was shown to reach equilibrium in 120 min. in diffusion experiments, requires a similar time for the fall of resistance in the second period.

Also, Haly [3] has shown that the rate of diffusion of water into a fiber varies inversely with the fiber diameter squared. Hence we would expect the ratio of the diffusion rate for Corriedale fibers (50μ diameter) to that for horsehair (200μ diameter) to be approximately equal to the inverse ratio of their respective diameters squared; i.e. 16:1. The experimental results (Figures 3, 4) show that the fall of resistance in the second period, which we have assumed to be due to water vapor diffusion, takes

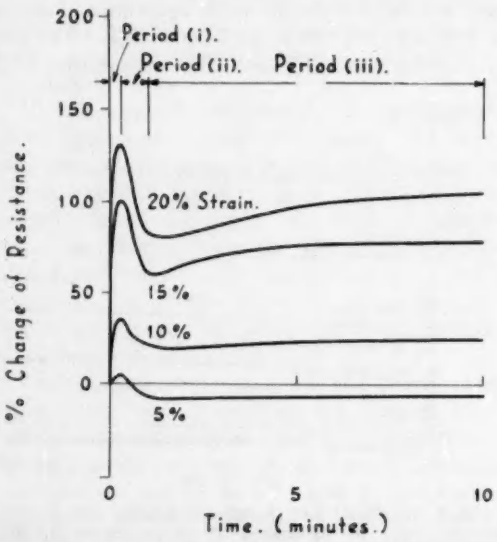

Fig. 4. The change of resistance with time for Corriedale fibers after the application of various strains at 90% RH, 19.6° C.

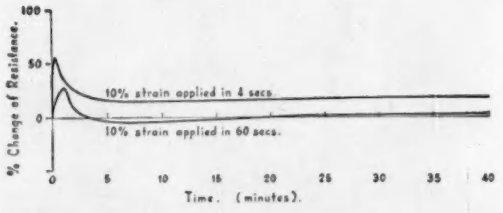

Fig. 5. The change of resistance with time for horsehair subjected to 10% strain applied at two different rates at 90% RH, 19.6° C.

place for Corriedale fibers in 0.7 min. and horsehair in 10 min.; i.e., in a ratio 1:15.

Furthermore, Treloar [13] has shown, using a thermodynamic argument, that horsehair fibers should take up water vapor in proportion to the applied stress, and he proved experimentally that, at 75.5% RH, horsehairs experienced an increase in weight when under a constant applied stress. The stress which he used was equivalent to that produced in horsehair by a 2% strain when the rate of straining is 150%/min. as used in the experiments reported in this paper.

If it is assumed that the fall of resistance in the second period is *entirely* due to an increase in the moisture content and that the fiber resistance still follows the same slope of resistance/moisture content as indicated in the results of Marsh and Earp [6], we can obtain approximate values for the amount of moisture uptake for a 2% strain in horsehair. When allowance has been made for the amount of moisture which has entered the fiber during the straining period and the period caused by the finite time constant (35 sec.) of the recording apparatus (by extrapolation of the 2% strain curve in Figure 3 (bottom)), we obtain an increase in moisture content of approximately 0.3%. This figure is in reasonable agreement with Treloar's result; i.e., for a stress corresponding to a 2% strain, an increase in moisture content = 0.25% ± 0.06%.

The rise of resistance in the third period of the resistance/time graphs (Figures 3, 4) is thought to be due to the fact that excess water is leaving the fiber. This would occur if the rate of diffusion was greater than the rate of stress relaxation. Since all the fibers had practically the same rate of stress relaxation, the greatest rise of resistance occurs with the Corriedale fibers, while there is only a small rise in the case of the horsehair and none at all for the silicone-covered fiber, which has a diffusion rate less than the rate of stress–relaxation. The fact that, within experimental error, the resistance decreases by amounts of the same order for all strains from 5% to 20% is probably due to the equal amounts of stress–relaxation which follow the application of strains from 5% to 20% (Figures 6, 7).

It is worth noting that the curves of Figures 3 and 4 are almost identical in form to those of the increase in moisture content/time curves, since for small changes in moisture content the decrease of resistance is linearly related to the increase in moisture content.

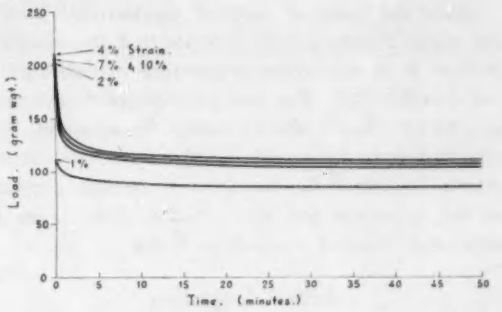

Fig. 6. Stress–relaxation for horsehair at 90% RH, 19.6° C.

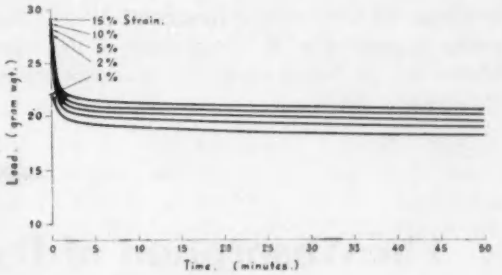

Fig. 7. Stress–relaxation for Corriedale fibers at 90% RH, 19.6° C.

Conclusion

Observations of the change of resistance with time, after a strain has been applied, at 90% RH and 20° C. for horsehair and Corriedale wool indicate:

1. There is a definite initial increase of resistance related to the applied strain. It is much larger than that due to the dimensional change.

2. There is a decrease in resistance, which takes place at the same rate as that of the diffusion of water vapor into the fiber.

3. There is an increase in resistance at a later period, caused by the difference in the rates of stress–relaxation and water vapor diffusion.

4. If it is assumed that the drop in resistance (No. 2 above) is due only to a change in moisture content, then the observed resistance decrease corresponds to an increase in moisture content approximately equal to that required by the theory of Treloar in the linear viscoelastic portion of the fiber stress–strain behavior.

From the point of view of conductivity theory, the above results merely indicate that the moisture content is of paramount importance in determining the conductivity. The strain–resistance relationship mentioned (No. 1 above) cannot be accurately determined from the results of these particular experiments, because of the limitation of the time constant of the apparatus and the different times taken to apply the required strain in each test.

Acknowledgments

This work is to be submitted in partial fulfilment of the requirements for the degree of Master of Science from the University of New South Wales. The author is grateful to M. Feughelman of the above laboratories for helpful advice and discussion during the course of the work.

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Manuscript received September 17, 1958.

The Absorption of Dyes by Cellulose Acetate from Nonaqueous Media[1]

Calvin Heit, Mary Moncrieff-Yeates, Ann Palm, Mildred Stevens, and Howard J. White, Jr.[2]

Textile Research Institute, Princeton, New Jersey

Abstract

Results are given for the absorption of three disperse dyes by secondary cellulose acetate from solutions in benzene at 25° C. and 35° C. Additional results are given on the absorption of one of the dyes from solutions in methanol, butyl acetate, and carbon tetrachloride at 25° C. Formally the isotherms can be well represented by Langmuir's equation.

The results obtained using different solvents show that, in general, the solvents do not act as inert transfer media but effect the basic absorption process for the dye. It is shown that the results can be explained if it is assumed that some solvents compete with the dye for absorption sites within the fiber.

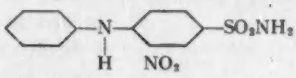
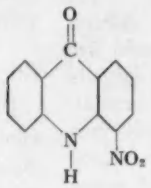
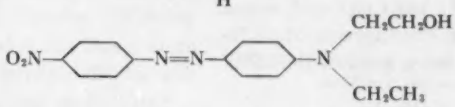
Introduction

With the advent of a variety of hydrophobic synthetic fibers, the disperse dyes, which were originally synthesized for the dyeing of cellulose acetate, have become of increasing importance. The name derives from the fact that these dyes are applied from an aqueous dispersion rather than from a true solution, since the dyes are only slightly soluble in water. It is characteristic of these dyes that the rate of dyeing depends, in part, on the size of the dispersed particles.

[1] Presented before the Polymer Division at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 13, 1955.

[2] All communications regarding this article should be directed to H. J. White, Jr.

TABLE I. Dyes Used

Designation	Structure	Color
Sulfonamide		Yellow
Acridone		Yellow
Azo		Red

Because of the complex nature of the practical dyebaths, various measurements have been made using simplified systems. Thus Bird and coworkers [2] and Majury [3] have studied the uptake of dye from true aqueous solution at temperatures in the range 50–100° C., and Majury [4] has studied the uptake of dyes from the vapor.

The work reported in this paper is concerned with the uptake of dyes from true solution in organic liquids. Three different dyes were used with benzene as solvent, and three other solvents were used with one of the dyes. Absorption isotherms were obtained using cellulose acetate as the substrate. The isotherms were obtained at 25° C. and, in some cases, 35° C. In some instances the solubility of the dye was also measured.

Materials and Methods

Cellulose Acetate

The cellulose acetate used was a conventional secondary cellulose acetate yarn spun without the usual finishing oil, which is difficult to remove and may interfere with the spectrophotometric measurement of the dye content. The samples were extracted with benzene and then dried in air at 110° C., then in a vacuum desiccator over magnesium perchlorate to constant weight. The drying at 110° C. was of short duration and designed to speed up the overall drying process without damaging the sample.

Dyes

The dyes used are shown in Table I. They were recrystallized from benzene.

Solvents

The solvents used were benzene, carbon tetrachloride, methanol, and butyl acetate. Dried, redistilled, thiophene-free benzene and dried carbon tetrachloride were used. The other solvents were used as received.

Dyeing Process

The samples were dyed in a constant temperature bath with sporadic agitation. The time of dyeing varied from 72 hr. to months, depending on the solvent. The samples dyed using benzene, methanol, or butyl acetate as solvent were placed directly into the dyebath. The samples dyed using carbon tetrachloride as a solvent were dyed in benzene to a dye content above the final value and then dried and brought to equilibrium in carbon tetrachloride by desorption.

Washing Process

It is necessary to wash the sample to remove entrained solution without removing absorbed dye. The washing was found to be satisfactory when an ~0.1 g. aliquot of the newly-dyed sample was blotted with filter paper, air dried for a few minutes, and then washed for 10 sec. in benzene at 6° C.

Analysis

The washed samples were dissolved in acetone and the dye taken up measured with a Beckmann DU spectrophotometer. In general the solutions followed Beer's Law; the presence of the small amount of cellulose acetate was found to be unimportant. The spectrum of dilute solutions of the azo dye in carbon

tetrachloride changed slowly, especially when illuminated, but not rapidly enough to cause serious trouble; all other solutions seemed to be stable. A standard error of 2–3% was obtained.

Solubility Measurements

The solubility measurements were made difficult by the ease with which small particles of solid dye were suspended in the solution. Solutions initially made at 45° C. and at room temperature were allowed to stand for 7 days in a thermostat and then centrifuged twice. The dye contents were measured spectrophotometrically and the runs repeated unless the dye concentrations were in close agreement. The solubilities are estimated as being good within 5%.

Discussion of Methods

Washing Process

In any measurement of this kind, the separation of entrained solution from absorbed material is difficult. Three types of measurement indicate that the washing process used was satisfactory. First, a microscopic examination of selected washed and dried fibers showed no crystalline dye on the surface from dried entrained solution and no light-colored surface layers from desorption of absorbed material. Second, in some cases the dye uptake could be checked by measuring the change of concentration of the dye solutions. In such cases the two methods agreed well. Finally, the process was found to be quite reproducible.

Proof of Equilibrium

Preliminary rate experiments were run to determine the amount of time necessary to ensure equilibrium. Equilibrium was reached relatively rapidly when the solvent was benzene, methanol, or butyl acetate and relatively slowly when carbon tetrachloride was the solvent.

Equilibrium was approached from both the absorption side and the desorption side at certain concentrations using benzene and butyl acetate as solvents; no hysteresis was found. Since methanol swells cellulose acetate appreciably, there is no reason to expect extremely slow absorption or sorption hysteresis with this solvent. Thus the results can be accepted as equilibrium results with these solvents.

When carbon tetrachloride was the solvent, predyed samples were placed into dye solutions. The dye content of the samples was slightly above the predicted equilibrium value for the solution. An experiment was also run in which the dye content of the sample was slightly below the equilibrium value. Samples removed after 15 and 29 days showed that dye was transferred from the bath to the fiber, although the changes of dye content of the fiber and of the bath fell within the experimental error of the measurements. Since a similar sample put into dye-free carbon tetrachloride for 10 days caused an in-

TABLE II. Uptake of Sulfonamide Dye from Benzene Solution at 25° C. and 35° C.

25° C.		35° C.	
Concentration, M/l. $\times 10^5$	Uptake, mM/g. $\times 10^3$	Concentration, M/l. $\times 10^5$	Uptake, mM/g. $\times 10^3$
0.80	1.90	4.58	6.90
1.29	2.90	5.37	7.70
1.58	3.60	6.80	10.4
2.57	5.80	7.15	11.7
2.80	6.10	7.83	10.6
3.02	6.50	11.4	15.2
3.90	8.50	14.4	26.3
7.39	14.3	15.8	24.3
8.35	16.6	17.3	30.7
10.2	16.9	17.5	30.7
12.5	23.8	26.4	35.0
14.4	26.5	27.3	41.4
17.2	32.1	29.5	38.4
21.0	36.5	33.4	45.8
24.6	41.7	36.9	45.7
29.1	49.3	38.2	42.3
29.8	51.7	40.4	47.2
29.9	52.0	41.6	51.3
35.6	58.1	42.2	48.9
39.1	60.4	43.9	49.4
44.0	70.7	45.3	54.4
46.7	73.8	48.2	56.8
49.3	74.6	49.9	55.4
52.2	79.3		
56.3	81.3		

TABLE III. Uptake of Acridone Dye from Benzene Solution at 25° C. and 35° C.

25° C.		35° C.	
Concentration, M/l. $\times 10^4$	Uptake, mM/g. $\times 10^3$	Concentration, M/l. $\times 10^4$	Uptake, mM/g. $\times 10^3$
5.00	2.30	6.65	3.08
11.1	4.82	6.83	3.27
11.6	4.68	11.1	4.76
16.2	6.42	16.3	5.82
21.9	8.60	22.3	8.50
22.0	8.16	25.5	8.76
22.4	9.16	26.8	9.81
26.3	10.7	37.8	12.3
32.0	11.5		
36.5	13.3		

TABLE IV. Uptake of Azo Dye from Benzene Solution at 25° C and 35° C.

25° C.		35° C.	
Concentration, $M/l. \times 10^4$	Uptake, $mM/g. \times 10^3$	Concentration, $M/l. \times 10^4$	Uptake, $mM/g. \times 10^3$
5.24	3.79	5.75	3.25
7.40	5.78	6.79	5.71
12.2	8.31	9.90	11.6
14.6	9.88	10.6	7.10
14.9	10.7	14.6	8.05
17.5	11.6	23.4	12.3
19.9	16.2	23.5	15.4
22.1	14.9	25.0	14.9
24.4	16.9	26.6	16.6
25.1	17.0	28.7	14.7
26.0	17.3	30.7	15.4
27.2	17.3	36.9	20.6
27.5	17.0	46.5	21.6
29.2	18.1	47.2	26.9
34.1	22.2	58.4	32.2
36.0	22.7	61.9	34.9
36.6	23.1		
46.0	26.4		
49.5	30.1		
50.0	29.7		
53.6	30.3		
54.9	32.2		
55.0	31.1		
57.0	31.6		
58.4	32.8		
61.0	34.1		
63.4	36.2		

TABLE V. Uptake of Azo Dye from Methanol Solution at 25° C. and 35° C.

25° C.		35° C.	
Concentration, $M/l. \times 10^4$	Uptake, $mM/g. \times 10^3$	Concentration, $M/l. \times 10^4$	Uptake, $mM/g. \times 10^3$
7.20	4.60	5.37	2.08
9.31	3.45	9.06	3.19
21.6	9.04	11.1	3.67
35.0	12.8	22.0	7.28
50.6	17.9	47.3	15.3
70.0	23.8	53.1	16.1
85.7	26.2	71.3	20.5
92.5	26.3	93.6	24.6

TABLE VI. Uptake of Azo Dye from Carbon Tetrachloride and Butyl Acetate Solutions at 25° C.

Carbon tetrachloride		Butyl acetate	
Concentration, $M/l. \times 10^4$	Uptake, $mM/g. \times 10^3$	Concentration, $M/l. \times 10^3$	Uptake, $mM/g. \times 10^3$
1.81	12.4	0.47	4.75
2.50	13.9	0.51	5.99
3.12	14.9	0.80	8.12
4.04	22.2	1.11	11.4
5.11	28.5	1.27	16.4
5.85	30.6	1.38	14.5
6.10	34.0		

crease in the dye content of the solvent which was outside the experimental error, it is evident that appreciable desorption could have occurred under the conditions of the experiment. Thus it seems likely that the true equilibrium curve for carbon tetrachloride as a solvent lies quite near the curve shown.

Microscopic examination showed complete uniform penetration of the fibers.

Results

The equilibrium uptake results are given in Tables II through VI. The solubilities are given in Table VII.

Discussion

Dye Solutions

A glance at Table VII shows that the dye solutions are, at most, a few hundredths molar in concentration. The optical densities of the solutions followed Beer's Law over the concentration range usable in the spectrophotometer. Since some measurements were made using a cell having 1-mm path. length, the usable concentration range covered all of the concentration range available for the sulfonamide and acridone dyes and a considerable portion of that for the azo dye. No sign of dimer or micelle formation was detected. It seems reasonable to assume that the solutions are dilute enough to behave ideally, so that the activity of the dye is directly proportional to the concentration.

Measurements Using Benzene

If the Langmuir isotherm is assumed to apply, the condition for equilibrium with respect to diffusion of the dye can be written

$$\mu^{\Delta}_{OD} + RT \ln \frac{n_D}{B - n_D} = \mu_{OD} + RT \ln N \quad (1)$$

where n_D represents the amount of dye absorbed, B the number of sites, N the mole fraction of the dye in solution, μ^{Δ}_{OD} and μ_{OD} standard free energies of the dye in the fiber and in the solution, R the gas constant, and T the absolute temperature. A plot of the reciprocal of N against the reciprocal of n_D should be linear if Equation 1 is followed. Such plots are quite linear for the results given here, and least-square lines have been fitted to the

plots. The constants pertaining to the use of benzene as solvent are collected in Table VIII; an example of the fit of the resulting absorption isotherms to the experimental values is shown in Figure 1.

As is well known, the nature of the reciprocal plot places disproportionate weight on the measurements made using very dilute solutions; these measurements are the most likely to be seriously in error. Visually acceptable fits of the results can be obtained with markedly different constants, so that no great significance can be attached to their magnitude.

TABLE VII. Solubilities of Dyes in Various Solvents at 25° C.

Dye	Solvent	Solubility, $M/l. \times 10^4$
Sulfonamide	benzene	5.7
Acridone	benzene	44
Azo	benzene	103
	methanol	94
	carbon tetrachloride	9.0
	butyl acetate	247

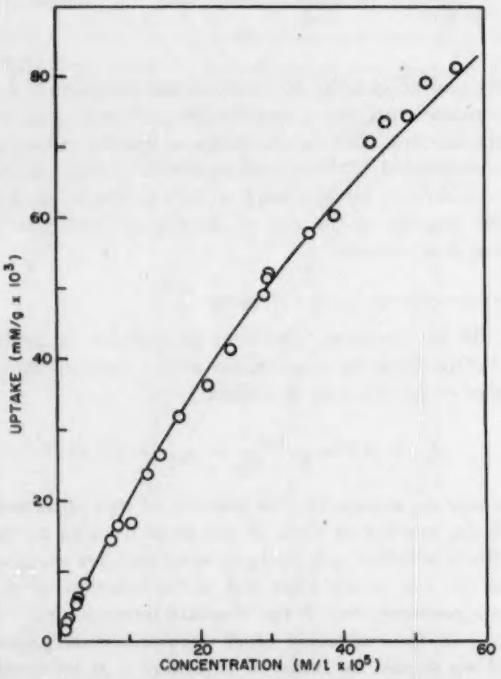


Fig. 1. Uptake of sulfonamide dye from benzene solution at 25° C. The curve represents Langmuir's isotherm.

Measurements Using Various Solvents

In considering the uptake of dye from different solvents, the problem of how to compare the solvents arises. It is clear that at a given temperature and pressure the partial molal free energy of the dye has the same value in all saturated solutions, namely, that of the solid dye. If concentration units are now expressed as percent of saturation, all solutions of a given percent of saturation will contain dye at the same partial molal free energy providing that the solutions are behaving ideally, as has been assumed to be the case with the solutions under consideration. Thus the uptake values will be plotted as functions of the percent of saturation.

If the absorption of the dye depends exclusively on the nature of the fiber and of the dye, the solvent functions only as a transfer medium. In such a case, all plots of uptake against percent of saturation should give the same curve, within the experimental error, regardless of the nature of the solvent. Such a plot for the experimental results for the azo dye is shown in Figure 2, and it is evident that a different curve is obtained for each solvent.

Either the solvent enters into the elementary absorption process (for example, by competing for sites with the dye) or it alters the nature of the substrate (for example, by swelling the fiber to open new sites). Some of the characteristics of the interactions of the solvents with cellulose acetate and with the azo dye are collected in Table IX.

Higher specific gravity values indicate penetration of the polymer by the solvent. The swelling values can be accepted only as approximations; they were made microscopically using a special round monofil. Water was included because of its technological importance, although no uptake measurements were made from water solutions because of the very small solubility of the dye in water at room temperature.

TABLE VIII. Langmuir Constants for Dyeing from Benzene Solutions

Dye	Temperature, °C.	B, mM/g.	$k_D' = \exp\left(\frac{\mu_{OD} - \mu_{OD}^{A}}{RT}\right)$
Sulfonamide	25	0.21	12,500
	35	.23	7,700
Acridone	25	.049	1,100
	35	.027	2,200
Azo	25	.15	550
	35	.10	810

It is evident that the highly penetrating, strongly swelling solvents are less efficient transfer media than the more inert solvents. This fact suggests competition between the dye and the solvent for absorption sites within the fiber. Presumably the same forces which cause the solvent to be a good swelling agent for the polymer cause it to interfere with the uptake of dye.

If competition between the solvent and the dye is accepted, Equation 1, which takes no account of such a competition, is not applicable. The question then arises as to why the equation provides a good empirical fit of the results. To consider this question, assume that both dye and solvent are absorbed at the same set of sites in accordance with Langmuir's equation. The solvent can also be absorbed at other sites in other ways, as long as Langmuir's assumptions are not violated insofar as the dye-absorbing sites are concerned. In place of Equation 1 it is possible to write

$$\mu^{\circ}_{D} + RT \ln \frac{n_D}{B - n_D - n_S} = \mu_{OD} + RT \ln N \quad (2)$$

$$\mu^{\circ}_{S} + RT \ln \frac{n_S}{B - n_D - n_S} = \mu^{\circ}_{S} + RT \ln (1 - N) \quad (3)$$

where n_S is the amount of solvent absorbed on the dye-absorbing sites, μ°_{S} and μ°_{OS} are free energies for solvent in a standard absorbed state and in the liquid respectively, and the other terms are as defined. Equations 2 and 3 can be combined to give

$$\frac{n_D}{B} = \frac{N}{\frac{1}{k_D'} + \frac{k_S}{k_D'} + N\left(1 - \frac{k_S}{k_D'}\right)} \quad (4)$$

TABLE IX. Interaction of Cellulose Acetate and Azo Dye with Various Solvents

Solvent	Uptake of dye at ½ saturation, mM/g. $\times 10^3$	Solubility of dye, M/l. $\times 10^4$	Sp. gr.* of C.A. in solvent, g./cc.	Cross-sectional swelling, %
Benzene	30	100	1.363	7†
Carbon tetrachloride	26	9	1.306	3.5†
Methanol	16	94	1.397	45†
Butyl acetate	14	250	1.382	≥ 26†
Water	—	~0.01	1.366	20?

* Fortess, F., TEXTILE RESEARCH JOURNAL 19, 23 (1949).
† Cates, D. M. and McCurdy, N. S., Textile Research Institute, unpublished results.

where

$$k_S = \exp\left(\frac{\mu^{\circ}_{OS} - \mu^{\circ}_{OS}}{RT}\right)$$

which has the same functional dependence of n_D on N as Equation 1 if $k_S/k_D' < 1$.

Because of the active participation of both components of the dyebath in the absorption process, there is little to be gained in determining apparent heats of absorption of the dye by the Clapeyron method.

Kinetics

No quantitative kinetic measurements were made; however, certain qualitative aspects of the absorption

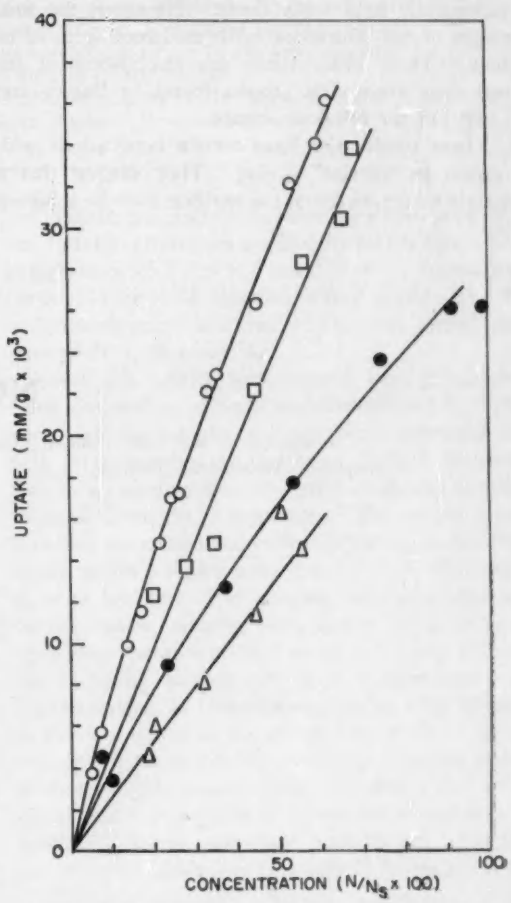


Fig. 2. Uptake of azo dye from various solvents at 25° C. as a function of degree of saturation. ○ = benzene, □ = carbon tetrachloride, ● = methanol, and △ = butyl acetate.

kinetics may be of interest. As has been mentioned, absorption from carbon tetrachloride solutions is very slow. Attempts to follow absorption from isooctane solutions were abandoned because of the unacceptably slow rate of absorption. Isooctane does not penetrate cellulose acetate, and carbon tetrachloride penetrates it only slightly. Thus some swelling of the fiber is apparently necessary for a reasonable rate of absorption at room temperature. Absorption from benzene, which is next among the solvents in order of swelling power, proceeds quite rapidly. In fact, equilibrium is apparently achieved somewhat more rapidly from benzene solutions than from methanol solutions. Actually, the initial reaction of the fibers to methanol is so rapid that methanol cannot be used successfully as a wash liquid. However, the final stages of the interaction with methanol seem to be slow. These observations are reminiscent of the two-stage absorption process found by Bagley and Long [1] for cellulose acetate.

These results also have certain implications with respect to "carrier" dyeing. They suggest that a certain minimum amount of swelling must be achieved but that swelling beyond that point may be unnecessary or even undesirable.

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NOTE

The address of Mr. John Boulton (December 1958) should be Courtaulds Limited, Droylsden, Manchester, England.

Comparison of the Mechanical Properties of Cotton Yarns and Fabrics Treated with Anhydrous Ethylamine and with Mercerizing Caustic

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Abstract

Samples of cotton yarn, tire cord, and fabric were subjected to treatment with anhydrous ethylamine to produce cellulose III. The physical and mechanical properties of these products were compared with those of the untreated materials (containing cellulose I crystal lattice) and of mercerized cotton (containing cellulose II crystal lattice). The ethylamine treatment produced effects upon the textile properties of the original materials which were similar to those of slack-mercerization but smaller percentagewise. The properties of the treated cottons apparently were affected more by the accompanying fiber swelling and yarn shrinkage than by the shift in crystal lattice.

Ethylamine-treated bandage gauze compared favorably with the slack-mercerized "conforming bandage" pioneered at the Southern Regional Research Laboratory.

IT HAS now been established that the treatment of cotton cellulose with anhydrous liquid ethylamine may yield either of two products. If the residual amine is extracted with a nonpolar solvent, the product is one of reduced crystallinity whose principal component is cellulose I [10, 11]. On the other hand, removal of the excess amine by evaporation results in a product which has cellulose III as its crystalline component [9]. The properties of textile materials containing cellulose I of reduced crystallinity have been reported elsewhere [10, 11]. However, since no report has been made in the literature concerning the physical properties of textile materials containing cellulose III, there is little evidence of their usefulness for practical textile products. It has been the purpose of the present study, therefore, to determine the important physical properties of textile products containing cellulose III, to compare them with the properties of those containing cellulose II (i.e., mercerized cotton) and with those containing cellulose I (i.e., the untreated control), and to indicate its potential value, if any, for textile use.

Materials and Methods

The anhydrous liquid ethylamine used in the present study was obtained by distillation of the commercially available product in an all-glass system.

Cellulosic materials included: (1) a low-twist 29.5 tex (20/1) cotton yarn purified by kier-boiling; (2) a high-twist 25.7 × 4 × 3 tex (23/4/3) cotton tire cord; (3) 28 × 24 bleached cotton gauze; (4) 48 × 48 cotton print cloth; and (5) desized, kiered, and scoured 80 × 80 print cloth.

Yarns and fabrics were treated with ethylamine using the method of Segal and coworkers [9]. The yarn and one sample of gauze were immersed for 4 hr. in anhydrous ethylamine at ice-bath temperature in a closed system; the print cloth was allowed to stand overnight in the amine. The excess amine was then removed from each material by distillation. Other gauze samples were treated with ethylamine in open beakers. The samples were immersed for varying times, ranging from 2 min. to 4 hr., and upon removal were allowed to air-dry under a hood. Some similar experiments were carried out with liquid ammonia and liquid methylamine. The amount of amine retained by the gauze, the extent of recoverability of the amine, the shrinkage, and the elastic recovery of the products were measured, and x-ray radial traces were made of the untreated and treated specimens before and after autoclaving. Samples were autoclaved for 20 min. under 15 lb./sq. in. steam

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

pressure (121° C.) to simulate the conditions of ordinary hospital sterilization.

Throughout this report, the term ethylamine treatment signifies immersion in ethylamine followed by evaporative removal of the residual amine, irrespective of the extent of conversion of the crystalline lattice.

For comparative purposes, samples which had been subjected to treatment with sodium hydroxide solutions of mercerizing strength (cellulose II) were carried along with the untreated control (cellulose I). Specimens were slack mercerized and mercerized under tension (to simulate commercial conditions). The slack-mercerized yarns were prepared by treating for 45 min. with 20% NaOH at 20° C., washing, neutralizing with 1% acetic acid, washing, and drying. The yarn mercerized under tension was treated at constant length for 3–4 min. with 23% NaOH, washed, neutralized with 3–5% acetic acid, washed, and oven-dried. Fabric was treated at constant length and width for 10 min. with 23% NaOH. Slack-mercerized gauze samples were prepared in the manner described by Goldthwait [2] for the elastic bandage.

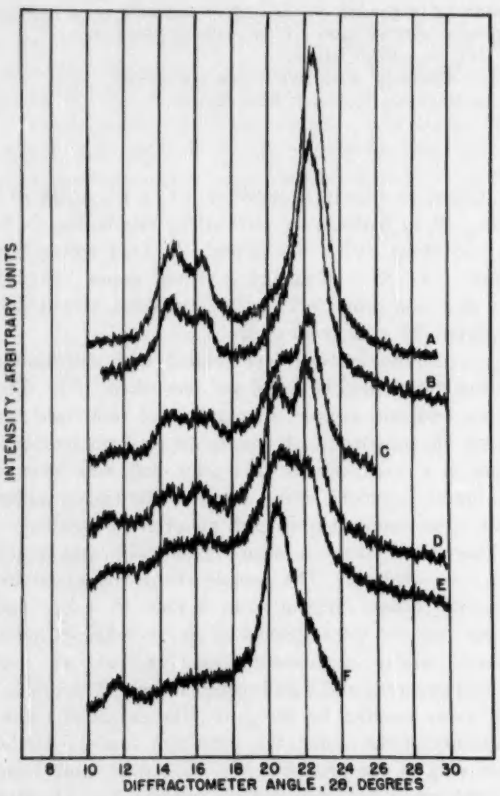

Fig. 1. X-ray radial tracings showing effect of textile construction upon the conversion of cellulose I to cellulose III by treatment with anhydrous ethylamine. A: Untreated (cellulose I); B: 25.7 × 4 × 3 tex (23/4/3) Delfos tire cord; C: 80 × 80 print cloth; D: 48 × 48 print cloth; E: 28 × 24 bleached cotton gauze; F: 29.5 tex (20/1) cotton yarn.

Radial traces of the x-ray diffraction patterns (CuK α radiation) were obtained for the untreated and treated samples using an x-ray diffractometer equipped with Soller slits. Specimens were ground in a Wiley mill to pass a 20-mesh screen and were compressed into a $\frac{1}{2}$-in. disc. The samples weighed 0.125 g. More complete details of the instrument and the procedure may be found in another publication [9].

The degree of polymerization (DP) for the untreated and treated materials was determined from cuprammonium fluidity measurements [1d, 13]. The intrinsic viscosities of the cellulose dispersions (concentration = 0.5 g./dl.) obtained from the relationship

$$[\eta] = 1.70\eta_{sp}^{0.694} - 0.160$$

were multiplied by the factor 260 to give the degree of polymerization. Crystallite length as indicated by the levelling-off degree of polymerization (LODP) was determined by the method of Nelson and Tripp [6].

Tensile tests on the yarn were made using the IP-2 inclined plane tester [2] (gauge length = 10 in.). The results were expressed as tenacity in grams per tex, and elongation was expressed as a percentage of the original gauge length.

Elastic recovery of yarns was also measured with the IP-2 tester. Elastic recovery as defined by Meredith [4] and Smith [12] is the ratio of recoverable strain to the total strain at any given stress. In these tests, cyclic stress–strain curves were obtained using 50% of the breaking strength as the maximum loading and a gauge length of 20 in. The minimum loading was zero stress with instant reversal of the machine. Yarns were cycled nine times and on the tenth cycle were carried to rupture. Recovery of gauze samples was measured with the aid of the "ruler test" [2]. This test consists of

[2] The mention of trade names does not constitute endorsement by the United States Department of Agriculture of one test instrument over those of other manufacturers.

applying tension sufficient to produce a 2-in. extension in a 10-in. specimen of the gauze (20% elongation). The tension is released and that portion of the 2 in. which is recovered is defined as the elastic recovery of the specimen.

Yarn number and twist were measured according to the standard ASTM procedure [1c].

Water retention of the materials was measured using the centrifugal method of Welo et al. [16]. Yarn and fabric samples were immersed in boiling water for 5 min., allowed to stand overnight in water, and then centrifuged. The percent water retention is defined as the intercept obtained by extrapolation to zero speed of the graph of water retained vs. the square of the speed.

Heat resistance studies on ethylamine-treated yarns, and the fibers obtained by defibering the treated yarns, followed the method of Moore [5]. The samples were heated in an oven at 160° C. for 16 hr. Tensile data on 10-in. yarn specimens were obtained using the IP-2 inclined plane tester. Fibers were tested on the Stelometer [2] at $\frac{1}{8}$-in. gauge length using the method of Orr, Weiss, and Grant [1h, 12].

Weight, warp and filling counts, strip breaking strength, and elongation at break of the fabric samples were determined according to the standard ASTM procedure [1a]. Tear resistance was measured using the Elmendorf [2] tear tester [1g]. Resistance to flex and to flat abrasion was determined using the standard ASTM procedure [1f]. "Dry" and "wet" Accelerotor [2] tests [13, 14] were also included. For these particular tests, weighed fabric specimens were abraded for 3 min. in the chamber, using the abrasive liner for the dry test and the metal ribbed collar and soap solution for the wet test. The tested specimens were then brought into moisture equilibrium for testing [1b], reweighed, and the weight loss calculated.

Air permeability was measured with the Permeometer [2] according to the standard ASTM technique [1e]. Weather resistance was investigated by exposing samples of fabric for a period of ten months with tensile properties being tested bimonthly.

Results and Discussion

Physical and Chemical Examination

The x-ray diffraction tracings shown in Figure 1 indicate that the extent of conversion from cellulose I to cellulose III is governed by textile construction. In the case of the high-twist tire cord, only the characteristic peaks of cellulose I—those at $2\theta = 14°$, 16°, and 22.6°—are present, indicating that no conversion was obtained. On the other hand, tracings from the treated fabrics indicate the presence of mixed crystal lattices. The presence of cellulose III is characterized by the appearance of peaks at $2\theta = 11.4°$ and 20.4°. It is assumed that the greater the height of these peaks, the greater is the extent of conversion to the cellulose III lattice. Thus, in the case of the fabrics, the more tightly woven 80 × 80 cloth exhibited the least conversion and the loose-weave 28 × 24 gauze the best. It is also apparent that almost complete conversion was obtained with the low-twist yarn. An attempt was made to obtain a quantitative measure of extent of conversion from peak–height relationships, but no significant trend was observed in the data. However, the effects observed strongly suggest that the tighter structures inhibit the penetration of the amine into the fine structure of the fibers, thus inhibiting the formation of the ethylamine-cellulose complex necessary in the conversion of the cellulose I lattice

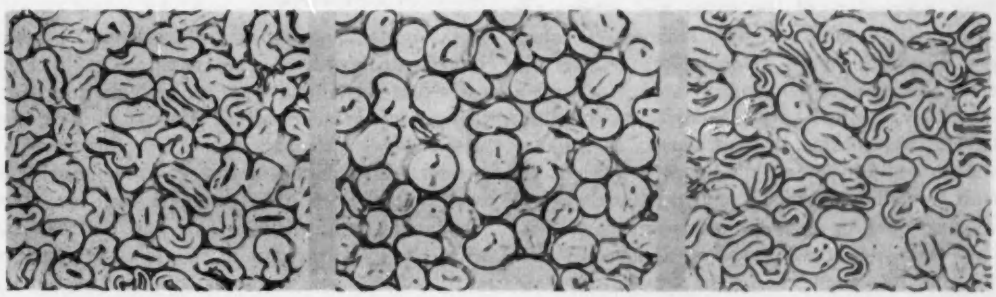

Fig. 2. Cross sections of untreated and treated cotton fibers. A: Untreated cotton (cellulose I); B: cotton mercerized slack (cellulose II); C: cotton treated with anhydrous ethylamine to produce cellulose III.

TABLE I. Degree of Polymerization (DP), Leveling-Off Degree of Polymerization (LODP), and Water Retention of Untreated and Treated Cotton Yarns and Fabrics

	29.5 Tex (20/1) yarn				80 × 80 Fabric			
Parameter	Untreated	Treated with ethylamine	Slack mercerized	Mercerized under tension	Untreated	Treated with ethylamine	Slack mercerized	Mercerized under tension
DP, anhydroglucose units	4970	4291	3966	4356	3975	3844	3383	3452
LODP, anhydroglucose units	225	112	144	150	217	140	143	149
Water retention, %	38.0	41.8	51.2	44.8	33.5	32.6	39.4	35.8

TABLE II. Mechanical Properties of Untreated and Treated 29.5 Tex (20/1) Cotton Yarn

Sample	Untreated	Ethylamine treated	Slack mercerized	Mercerized under tension
Cotton yarn no.	20.0	18.7	14.9	19.0
Yarn no., tex	29.5	31.6	39.6	31.1
Twist, turns/in.	13.5	14.3	16.1	12.6
Linear shrinkage, %	—	9.8	21.5	—*
Tenacity at break, g./tex†‡	14.9 ± 0.2	15.4 ± 0.2	14.0 ± 0.3	15.9 ± 0.5
Elongation at break, %‡	8.4 ± 0.1	13.6 ± 0.3	22.5 ± 0.7	5.6 ± 0.1
Elastic recovery, %‡	22.2 ± 0.3	14.2 ± 0.3	9.3 ± 0.1	32.1 ± 1.4

* Yarn held to original length during mercerization.
† Tex = g./1000 m. = 10 grex.
‡ Means and standard errors for 10 observations except for tenacity of untreated yarn, which is mean of 50.

to cellulose III. A similar effect of tension [3, 8] and textile construction [8] on inhibiting the conversion of cellulose I to cellulose II in the mercerization process has already been reported.

Microscopic examination revealed a swelling of the fiber cross sections by treatments which change the lattice type (Figure 2). It can be seen from the photomicrograph in Figure 2 that treatment with ethylamine produced fibers in which the lumens are more open but whose shapes remain elliptical, resembling those of the untreated control (cellulose I). On the other hand, slack mercerization (and mercerization under tension) produced fibers with closed lumens and nearly circular shapes.

Other parameters of the yarns and fabrics are summarized in Table I. Slightly reduced DP values suggest that little or no oxidative degradation has occurred because of ethylamine or mercerization treatment. Crystallite length, however, as indicated by LODP, was considerably shortened. In the case of the yarns, ethylamine treatment produced the shortest crystallite length, 112 anhydroglucose units; the higher values for slack and tension mercerization, 144 and 150 respectively, are not significantly different from one another. In the fabrics, all three treatments reduced crystallite length to approximately the same level, although tension mercerization produced a slightly higher value. These results indicate that textile construction and/or the presence of tension in the material strongly influence the extent to which fine structure is changed by complexing agents that penetrate the crystal lattice.

Water retention of the yarns was considerably higher after all treatments, and considerably higher than that of the treated fabrics. This, too, is in line with the fabric restriction and consequent incomplete transformation. The water retention of the fabric samples varied. It was increased by both of the mercerization treatments, but was unchanged by treatment with ethylamine.

Mechanical Properties

Yarns. Comparison of the mechanical properties of untreated and treated cotton yarns, Table II, indicates that ethylamine treatment and slack mercerization produced similar effects, although the percentagewise changes accompanying slack mercerization were greater. Considerable shrinkage occurred with both treatments, but the contraction in yarn length after ethylamine treatment was only half that associated with slack mercerization. Cotton yarn numbers were reduced as a result of both treatments; twist was increased, but tenacity at break relative to that of the untreated remained unaltered. There was a

significant increase in ultimate elongation, accompanied by a significant decrease in elastic recovery. Relative to the slack-mercerized yarn, the ethylamine-treated yarn had a lower extensibility but a higher elastic recovery.

Mercerization under tension produced a decrease in both cotton yarn number and twist. Although there was essentially no change in tenacity of the yarn, there was a 33% reduction in elongation at break. On the other hand, this treatment increased elastic recovery by 45%.

Heat resistance studies made on treated yarns, as well as on fibers obtained from them, showed that ethylamine treatment retarded the strength loss of fibers exposed to heat but had no effect upon such losses in yarns. These results are at variance with published data concerning the effect of liquid ammonia upon cotton (Table III), where strength loss was retarded in yarns but not in fibers [4].

Fabrics. Similarity of the effect of ethylamine and slack-mercerization treatments on textile properties is also seen in the data obtained on untreated and treated 80 × 80 cotton print cloth (Table IV).

TABLE III. Effect of Heating for 16 Hr. at 160° C. Upon the Strength of Untreated and Treated Fibers and Yarns

	Fibers		Yarns	
	Bundle tenacity*		Breaking load*	
Treatment	Unheated, %	Heated, %	Unheated, %	Heated, %
Control	100.0†	42.5	100.0†	23.2
Ethylamine treated	98.3	57.5	108.0	30.8
Slack mercerized (20% NaOH)	114.5	54.3	117.6	17.9
Tension mercerized (20% NaOH)	118.0	80.6	101.5	53.0
Data from Moore [5]				
Untreated	100.0‡	74.0	100.0‡	55.3
Liquid ammonia	94.0	79.0	106.4	87.6
12.5% NaOH	—	78.7	108.3	69.1

* Strengths are computed as a percentage of the unheated untreated control.

† Bundle tenacity of control = 18.6 g./tex. Breaking load of control yarn = 450.3 g.

‡ Bundle tenacity of control = 44.7 g./tex. Breaking load of control yarn = 1383 g.

Fabric shrinkages, reflected by higher thread counts and increased weight per unit area, were found to be approximately equal. Breaking strength, elongation at break, and tearing strength were significantly increased, and air permeability was greatly reduced. All of these changes are of the same order of magnitude; only in abrasion resistance were great differences found. The various abrasion tests indicated that ethylamine caused a reduction in abrasion resistance, whereas slack mercerization produced a fabric whose abrasion resistance was either as good as, or better than, that of the untreated.

Mercerization under tension had no effect upon fabric breaking strength, but caused a reduction in elongation at break. Tear and abrasion resistance were improved, and air permeability was greatly increased.

The apparent similarity of the effects of ethylamine and slack mercerization treatments seem to indicate that changes in yarn and fabric properties are influ-

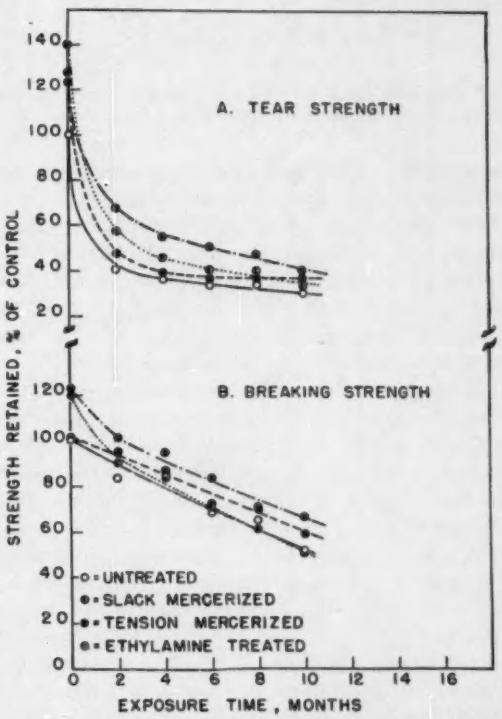

Fig. 3. Effect of weathering on tearing and breaking strength of treated 80 × 80 fabrics. A: Tearing strength; B: breaking strength.

TABLE IV. Textile Properties of Untreated and Treated 80 × 80 Cotton Fabrics

Property	80 × 80 Untreated	Ethylamine treated	Slack mercerized	Mercerized under tension
Linear shrinkage,* %				
Warp	—	13.3	15.7	—*
Filling	—	14.1	13.0	—
Count				
Warp	77.6	89.2	95.6	78.0
Filling	78.8	89.8	94.6	79.0
Weight, oz./sq. yd.	3.17	4.27	4.88	3.22
Breaking strength, warp, lb.	42.3 ± 0.5	51.9 ± 1.3	50.6 ± 0.5	42.5 ± 1.0
Tearing strength, warp, lb.	3.0 ± 0.1	3.8 ± 0.1	4.1 ± 0.1	3.6 ± 0.1
Elongation at break, warp, %	14.4 ± 0.0	30.6 ± 0.7	36.7 ± 0.7	12.0 ± 0.4
Abrasion resistance, warp				
Flat, cycles	50 ± 4	26 ± 1	40 ± 4	46 ± 4
Flex, cycles to rupture	841 ± 37	406 ± 10	3038 ± 86	1360 ± 67
Accelerotor, % loss of wt.				
Dry test	3.3 ± 0.1	2.8 ± 0.0	3.2 ± 0.1	3.2 ± 0.1
Wet test	1.4 ± 0.1	1.6 ± 0.0	1.6 ± 0.0	0.7 ± 0.1
Air permeability, ft.³/min./ft.²				
Dry: before Accelerotor	123 ± 4	44 ± 2	18 ± 0.5	198 ± 1
after Accelerotor	128 ± 3	69 ± 2	44 ± 0.4	159 ± 3
Wet: before Accelerotor	125 ± 3	40 ± 1	19 ± 0.7	177 ± 6
after Accelerotor	89 ± 4	90 ± 2	49 ± 2	159 ± 3

* The fabric was held to original length and width during mercerization.

enced more by fiber swelling and accompanying yarn shrinkage than by type of crystal lattice.

The effect of weathering upon the tensile and tearing strength of the various fabrics exposed at New Orleans, Louisiana for a period of ten months, extending from June 27, 1955 through April 27, 1956, is shown in Figure 3. It can be seen that the strength retained by the amine-treated fabric when based upon the control was greater than that of the other specimens. The same is true of tear resistance.

The apparently equal shrinkages of 80 × 80 fabric caused by ethylamine and by slack-mercerization treatments led to a consideration of the effect of ethylamine upon a 28 × 24 bleached bandage gauze. According to Goldthwait [2], the elastic property of the conforming bandage prepared by slack mercerization is primarily due to the shrinkage which occurs upon treatment with caustic. From those observations it would follow that if ethylamine produced a similar effect upon gauze, it might be substituted for sodium hydroxide in the preparation of such a bandage. The principal advantages to be gained would lie in omission of the necessary washing and drying steps of the caustic process and in recoverability and re-use of the amine.

Shrinkage and elastic recovery data obtained from amine-treated and slack-mercerized gauze samples, before and after autoclaving, are compared in Figure 4. It can be seen from the data that, prior to autoclaving, shrinkage of the gauze was not influenced by the time of immersion in the amine, but that elastic recovery of the warp seemed somewhat time-dependent. That the gauze which had been treated for 4 hr. in a closed system showed less shrinkage than the corresponding sample which had been treated in an open beaker was undoubtedly due to restraining forces caused by folding of the former sample when it was placed in the treating chamber. Although equivalent shrinkage resulted after each of the other treatments, elastic recovery of the amine-treated samples was not as great as that obtained by caustic treatment. After autoclaving, however, the amine-treated samples showed different properties. Whereas shrinkage was essentially unchanged, elastic recovery was increased to the extent that these samples exhibited essentially the same recovery as the

slack-mercerized specimens. The clinging properties of the amine-treated gauze, that is, the ability of the fabric to adhere to itself when folded back upon itself, were as good as those of the slack-mercerized material.

Consideration of the x-ray data of Figure 5 in conjunction with the physical properties shown in Figure 4 suggests that the elastic properties of the ethylamine-treated gauze are primarily due to the shrinkage accompanying the treatment rather than to the presence of cellulose III. Although the presence of some cellulose III is indicated with even the shortest period of immersion prior to autoclaving, as shown by the shifts in the x-ray patterns of Figure 5, the corresponding physical data (Figure 4) seem to show an inverse relationship between elastic recovery and extent of conversion to cellulose III; that is, time of immersion. In addition, results after autoclaving, when the crystalline structure has been reverted to that of cellulose I, indicate greatly improved elastic recoveries which are equivalent to those obtained with mercerization, in which case the crystal structure is known to be cellulose II.

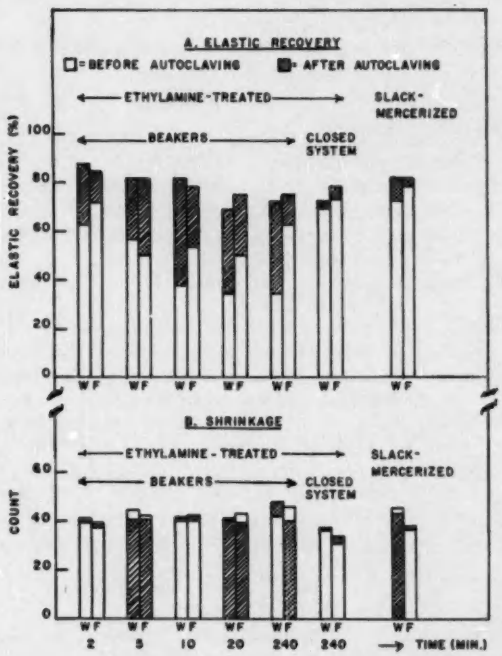

Fig. 4. Shrinkage and elastic recovery of ethylamine-treated and slack-mercerized 28 × 24 gauze samples before and after autoclaving.

The data indicate that 5 min. immersion time in the ethylamine was sufficient to produce a gauze with shrinkage and elastic recovery measurements comparable to those of the slack-mercerized. The amount of amine retained by a sample which had been immersed for 5 min. was small, only 0.75% before

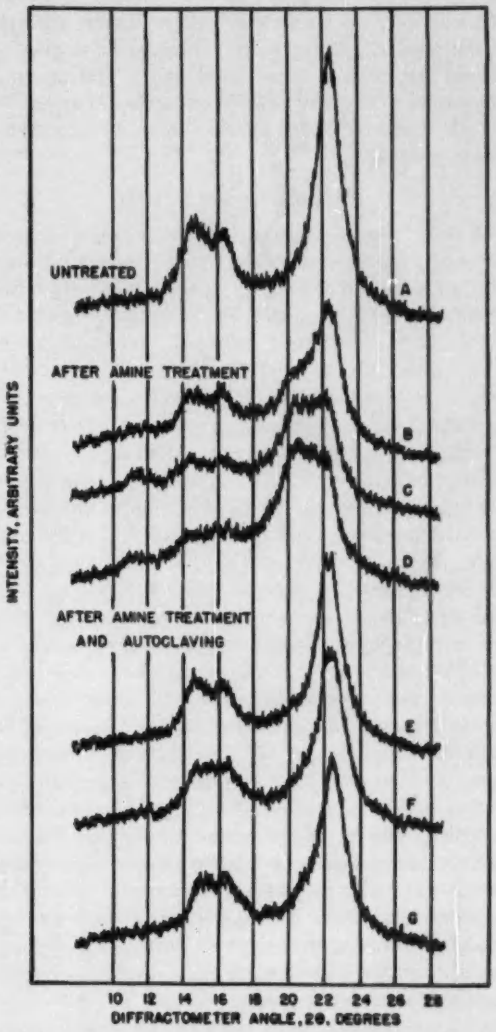

Fig. 5. X-ray diffractometer radial tracings of bleached gauze after various treatments with ethylamine. A: Untreated 28 × 24 gauze; B: immersed 2 min. in ethylamine in open beaker before autoclaving; C: immersed 4 hr. in ethylamine in open beaker before autoclaving; D: immersed 4 hr. in ethylamine in closed system before autoclaving; E, F, and G: amine treatments same as B, C, and D, respectively, but followed by autoclaving.

autoclaving. Some 96–99% of the original amine was recoverable for re-use. From this it appears that substitution of ethylamine for caustic is highly feasible. The over-all economics of the two processes are being studied.

Substitution of less expensive liquid ammonia for ethylamine resulted in a gauze with equal shrinkage but with very poor elastic recovery. Liquid methylamine produced a gauze with comparable elastic recovery but with a harsh hand and a stiffness not present in those treated with either liquid ammonia or ethylamine. These effects cannot be accounted for at present.

Summary

A study has been made of the mechanical and physical properties of cellulose III—the decomposition product remaining after cotton cellulose has been immersed in anhydrous ethylamine and the excess amine has been removed by evaporation. X-ray examination indicated that extent of conversion of cotton cellulose I to cotton cellulose III depends upon the textile construction being treated. Photomicrographs indicate that treatment with ethylamine, slack-mercerized as well as mercerized under tension, results in fiber cross sections of characteristic appearance—open lumens and elliptical shapes after ethylamine treatment, closed lumens and near circular shapes after mercerization.

Comparison of the physical properties of cotton cellulose III with those of cotton celluloses I and II indicated that, in general, ethylamine and slack-mercerization treatments produced similar changes in the properties of yarns and fabrics. Changes in yarn and fabric properties seemed to be influenced more by fiber swelling and yarn shrinkage than by crystal lattice type. Various abrasions tests indicated that ethylamine treatment resulted in a fabric with reduced abrasion resistance, while slack mercerization resulted in one whose abrasion resistance remained essentially unchanged or showed an increase over that of the control. Weathering experiments indicated that the strength retention based upon the control was greatest for the amine-treated specimens. Heat resistance studies of treated yarns and fibers showed that ethylamine produced a retarding effect upon heat-induced strength loss of fibers, but had no effect upon loss in yarn strength.

Bleached cotton gauze immersed in liquid ethylamine possessed elastic properties similar to those exhibited by the slack-mercerized conforming bandage of SRRL. Substitution of ethylamine for the sodium hydroxide solution used in the commercial mercerization process would eliminate the need for neutralizing, washing, and drying operations.

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Polyamine Resins for Finishing of Hydrophobic Fibers[1]

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Abstract

A finish designed to protect textiles in use against accumulation of static must possess hygroscopicity, high ionic concentration, and resistance to washing and drycleaning. Polyelectrolytes deposited from aqueous solution and cross-linked on the fiber are capable of fulfilling these requirements. Polyamines cross-linked by alkylation with polyhalides were selected to study the correlation between structure and antistatic performance. The gelling time of the polyamine/polyhalide mixture *in vitro* supplied an excellent indication for the suitability of the reactants to form durable antistatic finishes on the fiber. Some correlation between the degree of polymerization and branching of the polymers and their antistatic performance was established. The new class of polyamine resins promises to be a useful addition to available textile finishes.

Introduction

The investigation reported here was aimed at the elimination (by chemical means) of the occurrence of static electricity in the use of fabrics made from hydrophobic fibers; i.e., at the preparation of antistatic finishes resistant to repeated washings and drycleanings. Antistatic agents which are readily removed by the washing and drycleaning process have been on the market in large numbers and described in the literature. However, only very few antistatic agents are available possessing a measure of resistance to washing, and, aside from a few disclosures in the patent literature, publications concerning their structure are practically nonexistent.

Although there is no need to describe the phenomenon and drawbacks of static electricity in synthetic fabrics, it might be in order to describe briefly the concepts which guided the preparation and evaluation of durable finishes reported in this paper.

Dissipation vs. Generation

The magnitude of electrostatic charge of a body represents the balance between the rate of generation of the charge and the rate of its dissipation. It would therefore appear as feasible to reduce the charge by reducing the rate of generation as by increasing the rate of dissipation. A closer examination of the factors which determine these two rates indicates, however, the chemical control of the rate of dissipation is more practical than that of generation.

Attempts to correlate the generation of charges with chemical structure have not led to success, whereas the mechanism of charge dissipation and its dependence of chemical structure is fairly well demonstrated, as will be discussed below. Consisting in the transfer of ions and electrons from one body to the other when these are in contact, generation of charge depends on the ultimate surface of the bodies. This ultimate surface probably represents one or two molecular layers. The control of such surfaces is not easy, since the ever-present impurities tend to accumulate on them. This explains the difficulty in establishing the validity of the so-called electrostatic series even on a laboratory scale and in utilizing the existence of the series on a practical scale. Such a utilization was suggested for instance, for the production of electrostatically neutral fiber blends by appropriate mixing of positive and negative fibers. It is true that frictional and wetting properties of fibers, which likewise depend on the ultimate surface, are successfully regulated by finishing operations for the purpose of yarn softening and of water repellency, even though the reproducible measurement of these

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properties requires careful laboratory controls directed toward the exclusion of minute impurities. Both frictional coefficient and contact angle are determined by the average composition and structure of the surface layer, whereas it is not unlikely that the generation of charges depends on those few molecules present at the surface which show the greatest tendency to transferring charges. These circumstances could account for the fact that chemical modification of fiber surface has not proven successful in suppressing the tendency to generate the charges. On the other hand, the evidence in favor of a comparatively easy control of the tendency of the fiber to dissipate electrical charges is overwhelming. Electrical conductance (or its reciprocal value, resistance) measures the ability to dissipate charges. When the moisture content of natural hydrophilic fibers is reduced, they give rise to bothersome static phenomena as their conductivity decreases. Fibers of different types, arranged from hydrophilic to hydrophobic, show (at standard atmospheric conditions) increased electrical resistance and, parallel with it, increased tendency to exhibit static. The tremendous range of feasible variation of fiber conductivity contrasts sharply with the complete absence of data which would indicate a correlation between generation of charges and exhibition of static.

In this investigation the electrical conductance of the fibers is considered a measure of their tendency to accumulate electrical charges. Although accumulation of charges is the balance between their generation and dissipation, it was assumed in accordance with the conclusions reached by several other workers during the last 2–3 years [4, 6, 13, 20] that a sufficiently high electrical conductance will safeguard the fabric against the annoying and hazardous phenomena of static. The same assumption is implicit in the recommendation of the Antistatic Finishes Committee of the American Association of Textile Chemists and Colorists for using the electrical conductance of the treated fabric as a measure of the efficiency of antistatic finishes [2].

Conductance, Moisture Content, and Ionization

Efficient antistatic protection of textile fibers requires not only the presence of water (or other liquid of sufficiently high dielectric constant) but, in addition, the presence of electrolytes. The presence of water can be secured only through replenishment from the surrounding atmosphere. Thus, hygroscopicity and presence of ions are the dual requirements for the antistatic finish. A survey of the numerous available antistatic finishes [5] clearly reveals that these are of either hygroscopic or ionic nature or both. Since hygroscopic and ionizing compounds are usually water soluble, it is not surprising that most of the available antistatic agents are removable by washing.

The requirements for a durable antistatic agent, hygroscopicity and ionization on the one hand, insolubility on the other, appear almost contradictory. There is one answer—and probably only one—to this problem: the deposition of a hygroscopic and ionizable polymer on the surface of the fiber, the polymer insolubilized by cross-linkages between the macromolecules.

Polymer Structure and Durability of Finish

If we assume that the contribution of film surrounding the fibers to the conductance of the fabric is proportional to its thickness and that, on the basis of practical considerations, the finish cannot amount to more than approximately 1% on weight of the fabric, the conductance of the finish in bulk must be comparatively high. Postulating that the task of the antistatic finish is to raise the conductance of the fabric to the same level as that of hydrophilic fibers, e.g., cotton, at identical values of relative humidity, the finish in bulk must possess at least a hundred times higher conductance than cotton. Actually, probably due to lack of continuity of the finish film, its contribution will be less than that calculated from the bulk conductance, so that the required bulk conductivity must be even higher.

In querying about the forces which hold together durable finishes and fibers, a distinction can be made between systems which are held together by forces of adhesion such as covalent linkages between finish and fiber molecules or molecular attraction forces (substantivity) and systems which are held together by cohesive forces either of the finish or of the fiber [17]. The cross-linked polyelectrolytes discussed here belong to this latter category. The fact that they proved durable on such chemically dissimilar fibers as nylon, polyester, polyacrylonitrile, and glass indicates that the possibility of chemical reaction or molecular attraction between fiber and finish is remote and certainly not the main factor in their union. These finishes are to be visualized as forming concentric tubes around the individual fibers, as Fortess

[3, 21] demonstrated for the silicone finishes. Durability of such a finish against abrasion depends essentially on the mechanical properties of the finish in bulk.

The requirement of hygroscopicity, however, makes a finish particularly vulnerable to washing. The absorption of water, which functions as a plasticizer, reduces cohesion, i.e., the mechanical strength of the layer of finish surrounding the fiber. Therefore, wet abrasion during laundering becomes the determining factor for the durability of the finish.

Accumulation of hydrophilic groups in a cross-linked polymer will favor hygroscopicity, i.e., high moisture regain, but increasing tightness of the cross-linkages will tend to limit the ability of the polymer to absorb water. In order to be efficient, a hygroscopic film surrounding the fiber should possess the maximum moisture content at low relative humidities, but, in order to be resistant to washing, it should possess also a low water content when immersed in water. In general, however, high hygroscopicity at low relative humidity goes hand in hand with high hygroscopicity at high relative humidity, and thus a compromise must be found for a finish which is to combine efficiency with durability.

The second factor for conductivity, ionic concentration, is not limited by such a compromise. In absence of ions, the contribution of water would be comparatively small. In general, a fabric rinsed with water and dried will retain on its surface all the nonvolatile electrolytic impurities of the rinsing water remaining on the fabric after drainings. The effectiveness of nonionic antistatic agents is due to the presence of such tramp electrolytes [19, 20]. Many of the nondurable antistatic agents are of ionic nature, and their contribution to the conductance of the fibers is twofold: first, like most of the electrolytes, they are hygroscopic and therefore cause absorption of water; second, they supply the ions to provide the transportation of electric current. Without the presence of tramp electrolytes, a nonionic compound would not be useful as an antistatic agent, durable or nondurable.

In order to increase the contribution of a durable antistatic finish to the conductivity of the textile, it is desirable to provide for the presence of ions in a comparatively high concentration. The only means to achieve this is by the deposition of a cross-linked polyelectrolyte.

Conductance of Cross-Linked Polyelectrolytes

In the past few years, several papers were published on the electrical conduction of ion-exchange resins, and new theories were evolved based on the assumption of the mobility of the exchangeable ions [9, 10, 15]. Our investigation was based on the theory of M. E. Laing [8], published in 1924, in which a general formulation of movement in electrical field was proposed; it was shown that the phenomena of electrical conduction, electroosmosis, and electrophoresis are but special cases of an inherently identical process. As Scatchard has done recently [14], Laing considers the solvent as stationary in all these systems. Thus a direct relationship between the electrical conductance of a gel and that of its constituents is established, and the conductance of an ion exchange body can be related directly to the electrical conductance of the monomers which are polymerized to form it.

The close relation between the conductance of a sol and of the gel produced from it is valid as long as their concentration is the same. By reducing the relative humidity from 100% to lower values, the water content of the gel is decreased; in other words, the concentration of its solids is increased. As a consequence, the electrical conductivity decreases due to increased viscosity of the medium in which the ions are transported, decreased degree of ionization, and increased degree of discontinuity of the pathways of electrical current.

Assuming that this dependency is similar for the systems under consideration, a high ionic concentration of the monomers yielding high ion exchange capacity of the resins formed by their polymerization is likely to provide at all humidities a high surface conductance of the fabric finished by application of such a resin to the fabric.

Possible Polymeric Structures

There are innumerable possibilities open to produce cross-linked polyelectrolytes on the surface of fibers. The nature of the ionic groups can be varied from anionic (such as carboxylic, sulfonic, or phosphoric) groups to cationic (such as amine or sulfonium) groups; the cross-linking reaction can be varied from ethylenic (vinyl) or epoxy addition to condensation reactions yielding, e.g., ester, ether, ammonium, or urethane groups. Our exploratory experiments confirmed that suitable application conditions can be found for any of these possibilities.

For reasons which will be discussed later, we focused our attention on the possibility of utilizing amine groups for ionization and amine alkylation for cross-linking.

The following portion of the paper deals with the preparation of cross-linked polymers on the fiber and with the evaluation of their behavior as durable antistatic finishes.

Experimental

Antistatic efficiency of finishes was determined by measurement of the electrical conductance of treated fabrics. The electrical conductance of a fabric is expressed in terms of specific area resistivity (SAR). The specific area resistivity of a fabric means the resistance (in ohms) of a square-shaped piece of fabric between two parallel electrodes which form the boundaries of the square on opposite sides. As long as the fabric has a uniform composition, the specific area resistivity does not depend on the length and distance of the electrodes, which are equal. Assuming the same construction, the specific area resistivity is inversely proportional to the thickness of the fabric. For this discussion, the thickness of the fabric is considered constant, so that variations of the specific area resistance reflect only the variation of the chemical composition of the fabric (including, specifically, the chemical composition of the surface of fibers and yarns) but not of its construction and weight.

Unless otherwise specified, the conductance was determined at room temperature and 30% relative humidity. The fabrics were conditioned for at least 24 hr. before the measurement.

The amount of finish is given on the weight of the fabric (nylon, polyester, or triacetate). The fabrics treated were first carefully scoured and rinsed. Before treatment they were checked for absence of impurities by measuring their conductance. The treatments varied as to amount of finishing ingredient and drying and curing conditions, as specified.

Unless otherwise stated, the soluble polymer and the cross-linking agent were applied together from aqueous solution by simple padding on a three-roll laboratory padder.

Durability of the treatment was determined by change of the conductance after rinsing with water as well as after repeated washings and drycleanings. The washing was carried out in a Westinghouse "Laundromat" at 160° F. with 0.1% "Tide" as detergent and using the regular washing cycle with Jersey City tap water.

Polyamines in Textile Finishing

Among the fundamental reactions of ammonia and amines are those commonly described as acylation reactions and alkylation reactions. In the former type, the nitrogen of amines or even ammonia can be substituted easily with one acyl group only. In the latter type, four substituents can be introduced in the case of ammonia, three in the case of primary amines, two in the case of secondary amines, and one in the case of tertiary amines. Thus, a primary amine group may be defined as monofunctional in acylation reactions but trifunctional in alkylation reactions. This polyfunctionality of the amino groups allows them to become the junction points of a three-dimensional network under suitable alkylating conditions. The possibility of utilizing this principle for the preparation of durable antistatic finishes appeared attractive: the polymers resulting from this reaction would contain the ionizable groups required for effective and efficient antistatic performance, and the concentration of ionic groups could be controlled by the proper choice of raw materials.

When a compound containing two primary amino groups is reacted with an equimolar quantity of dihalide, soluble products may be obtained if the reaction is not driven too far. This indicates that the rate of alkylation of primary nitrogen to secondary nitrogen, according to the equation

$$x\mathrm{H_2NRNH_2} + x\mathrm{R'X} \rightarrow [\mathrm{—NHRNHR'}]_x + 2x\mathrm{HX}$$

is greater than the rate of alkylation of secondary nitrogen to tertiary. By employing excess dihalide, or more severe reaction conditions (time and temperature), or both, insoluble three-dimensional polymers can be obtained. The role of the excess dihalide in this insolubilization step is thus that of a cross-linking agent, alkylating the secondary nitrogen to tertiary nitrogen (or possibly to quaternary). From a general point of view, linear polymer initially formed and cross-linking agent are comonomers of a polycondensation reaction in which the linear polymer is polyfunctional. Arbitrarily, we considered here the dihalide as the cross-linking agent. In many polymeric systems, such as in the formation of urea-formaldehyde and phenolformaldehyde resins, linear polymers can be formed by control of monomer ratio and reaction conditions, then converted into

three-dimensional networks under more severe conditions. In others, such as alkyd resins, the formation of soluble and insoluble polymers is regulated by varying the ratios of mono-, di-, and trifunctional comonomers (mono- and dibasic acids, dihydric and trihydric alcohols). The alkylation of amines allows the application of these general principles of polymer chemistry. The preparation of polymeric amines and references to earlier literature were given by Kern [7].

While for application to textiles, the formation of insoluble polymers must be carried out on the fabric *in situ*, the study of the reaction *in vitro* is a useful guide for establishing conditions of application such as ratio of reactants, temperature, pH, etc. In such studies, gelation indicates insolubilization, or conversion of the product from the soluble (removable) type to the insoluble (durable) type. The identification of gelation in the test tube with fixation on the fiber was without doubt the most helpful simplification in this systematic search for durable finishes.

Two kinds of systems will be discussed: formation of insoluble polymers from polyfunctional amines and bifunctional alkylating agents in one step and preparation of soluble polymers from amines and dihalides as a first step, followed by cross-linking of these soluble polymers as a separate step.

In the application of urea formaldehyde systems to cellulosic fibers, monomeric materials can penetrate individual fibers, yielding results different from those obtained by application of soluble polymeric precondensates. In our case, we believe that the penetration of hydrophobic fibers remains insignificant even with monomeric compounds; the choice between the two possibilities is therefore entirely open, and must depend on other considerations.

Choice of Monomers

The selection of raw materials for the study of reactions of the first type was based on certain requirements which were considered important in order to transfer the results obtained *in vitro* to polymerization *in situ*.

In order to be carried out *in situ*, the reaction between dihalide and diamine must proceed at a rapid rate, yielding cross-linked products under comparatively mild conditions. While the temperature required for the polymerization reaction (which on the fabric becomes the curing temperature) should be below the temperature which would damage the fabric by melting, thermal decomposition, and discoloration, and while the curing time should not slow down processing below economical limits, it was also important that the polymerization should not proceed at appreciable rate at low temperature. The possibility of storing the impregnating solution in the processing tank for a number of hours, or preferably days, is an important requirement in the mill.

The impregnation of the textile should be carried out preferably from aqueous solution. Thus the raw materials, or monomers, employed should be water soluble. Almost any solvent other than water is expensive or flammable or toxic, often all three. Impregnation from emulsions is sometimes feasible, but emulsion stability on impregnation and drying would present additional problems. The decision to use water soluble materials imposed a definite limitation on the choice of monomers used.

The raw materials should not be volatile, since the loss of either reactant by evaporation during drying would alter the course of the polymerization reaction. The use of air-tight and/or pressure-tight equipment is not usually feasible in textile finishing plants.

It is obvious that all commercially successful finishing processes, including the polymerization of urea formaldehyde and melamine formaldehyde monomers, satisfy the requirements listed.

While many commercially available amines could be used in the framework of these requirements, the choice of the alkylating agent presented a somewhat more difficult problem. Commercially available dihalides are usually water insoluble and often volatile. The tendency to ring formation when a chain of less than eight atoms separates the halides or other alkylating groups leads to side reactions which hamper the course of polymerization. We found polyethylene glycol dihalides singularly suitable for our purpose: they are water soluble and nonvolatile, and the distance between halides can be readily varied between 8 and 100 atoms or more. An additional advantage of these materials is the presence of ether oxygen, which by virtue of hydrogen bonding contributes to the hygroscopicity of the resulting products.

On the basis of these considerations, certain pairs of comonomers were selected and applied to fabrics, using the results obtained by gelation experiments *in vitro* as a guide to application conditions.

Diethylenetriamine, hexamethylenediamine, and bis (3 amino propyl) amine were chosen as amine co-

monomer and poly (ethylene glycol) diiodide ($I(CH_2CH_2O)_nCH_2CH_2I$) as dihalide comonomer (cross-linking agent). The fabrics (nylon, Dacron,[4] polyester, and Arnel triacetate) were impregnated with the solution of the comonomers in equimolecular quantities to give a dry pick-up of from 1.8 to 5% on the weight of the fabric. The fabrics were dried at 50° C. for 10 min. and cured for from 5 to 40 min. at 150° C. In all cases initial specific area resistivity values considerably below that of cotton were obtained (log SAR of 9 against 12 for cotton), and the resistivity remained well below that of cotton even after 50 or 100 washings.

Based on the assumption that the reaction between diamines and dihalides would give first approximately linear polymers, it appeared feasible to carry out the polymerization reaction stepwise; to prepare first a linear, or approximately linear, soluble polymer which could be applied with the polyethyleneglycol dihalide as cross-linking agent to form the insoluble resin *in situ*. This is the second type of system to which we referred, and the following discussions will be limited to it. This type of reaction allows:

a. the preparation of a soluble polymer under controlled conditions, and thus better means of following the course of the reaction. The application of the products could then be carried out with somewhat less critical control of application conditions, and

b. the use of monomers which could be volatile or water insoluble, yet be fully practical if leading to linear polymer of satisfactory physical properties.

Correlation Between Structure and Performance

The effects of structural changes on performance were studied by variations in the following factors:

a. distance between the junction points of the network, controlled by selecting as comonomers, amines and dihalides in which the reactive groups were separated by chains of varying length, as well as by varying the distance between the halide groups in the cross-linking agent,

b. degree of polymerization (DP), controlled by the extent of the alkylation reaction and the ratio of comonomers, and

c. branching, controlled by the ratio of reactivity of the primary, secondary, and tertiary amino groups present or formed in the initial stages of the reaction.

[4] Du Pont trademark.

Effect of Distance Between Cross-Linking Sites on Performance

Soluble polymers were prepared from polyethylene glycol dihalides of varying chain length and amines of various types. The behavior of these polymers was studied with respect to the following properties:

a. rate of polymerization or cross-linking *in vitro*,
b. antistatic performance and durability on fabrics,
c. effect on the hand of fabrics, and
d. effect on the reflectance of white fabrics.

The polymers investigated belong to two types, in which the structure of the repeating units can be represented approximately as follows:

Type I $[—NH(CH_2CH_2O)_nCH_2CH_2NHR—]_x$

Type II $[—N(CH_2CH_2O)_nCH_2CH_2—]_x$ (R)

Polymers of Type I were prepared by reacting dihalides with amines containing two primary amino groups, and cross-linked by converting secondary nitrogen to tertiary nitrogen with a bifunctional alkylating agent. In polymers of this type, the frequency of the cross-linking sites was varied either by varying R, or by varying *n*, or both.

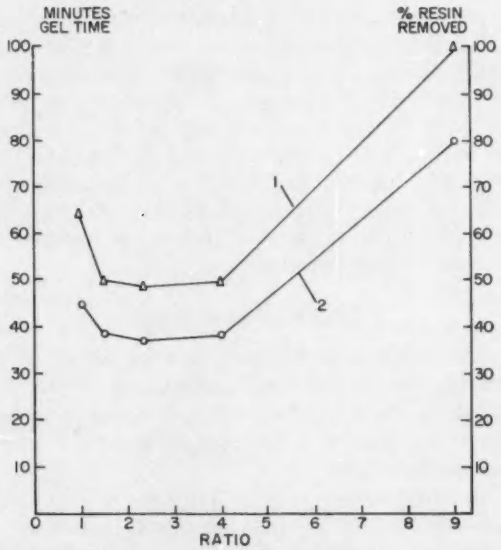

Fig. 1. Gel time *in vitro* (Curve 1) and removable resin on the fabric (Curve 2) as functions of the wt. ratio of polyamine (Type II) to cross-linking agent (Polyethylene Glycol 600 diiodide).

Polymers of Type II were prepared by reacting dihalides with amines containing one primary amino group, in approximately 1:1 molecular ratio, and cross-linked by converting tertiary nitrogen to quaternary nitrogen with a bifunctional alkylating agent. In polymers of this type, the distance between nitrogens can be varied only by varying *n*, even though the size and nature of the alkyl group R, which here forms the side chain, significantly affect the rate of the cross-linking alkylation reaction.

The rate of polymerization or cross-linking of these polymers was studied *in vitro* by determining the time required for gelation under carefully controlled conditions.

Figure 1 shows the excellent correlation between the amount of fixed finish on the fabric (here determined as percentage resin retained on the fabric after rinsing with water) and the time required to convert the monomers into a gel by heating in a test tube. The cure of the resin was carried out at 150° C. for 3 min. on a Dacron [4] fabric previously impregnated with the aqueous reactants (1% on the weight of the fabric) at pH 10 and dried. The gelation experiment was carried out at 90° C. in a 25% ethylene glycol solution at pH 10. The ratio of the reactants, namely polymeric tertiary amine of Type II and dihalide, was varied as shown on the graph.

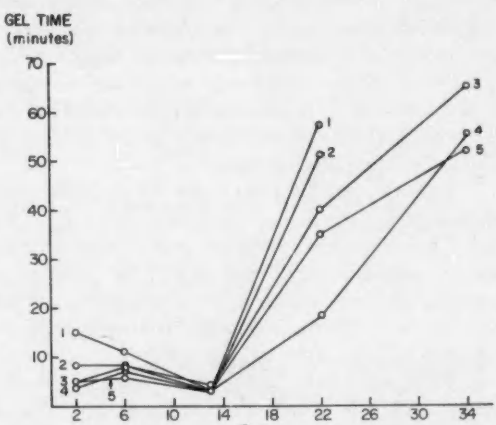

Fig. 2. Gel time as a function of *n* of polyamines (Type I) of formula

$[-NH(CH_2CH_2O)_nCH_2CH_2NHCH_2CH_2NHCH_2CH_2-]_x$

in mixture with cross-linking agent $I(CH_2CH_2O)_mCH_2CH_2I$ at a molar ratio of 3:1 (N:I), 150° C. and pH 10; 25% solids in ethylene glycol. Curve 1: $m = 2$; Curve 2: $m = 6$; Curve 3: $m = 13$; Curve 4: $m = 22$; Curve 5: $m = 34$.

By itself, this set of experiments would indicate only that a reactant mixture which sets faster *in vitro* gives more complete cross-linking on the fiber under the selected conditions of time and temperature. Our experience was, however, that the correlation extended far beyond this limit; invariably a faster gelling system, even under optimum conditions of cure, gave a resin which was more resistant to rinsing and also laundering, regardless of whether the reagent ratio, the pH, or even the chemical structure of the polymeric amine was varied. This might indicate that with slow gelling systems a side reaction (such as hydrolysis of the dihalide) tends to reduce the degree of fixation of the resin.

Figure 2 shows the experimental points obtained when the average value of *n* is plotted against gel time for polymers of Type I alkylated with five different cross-linking agents. Figure 3 shows the experimental points obtained when *n* is plotted against gel time for polymers of Type II alkylated

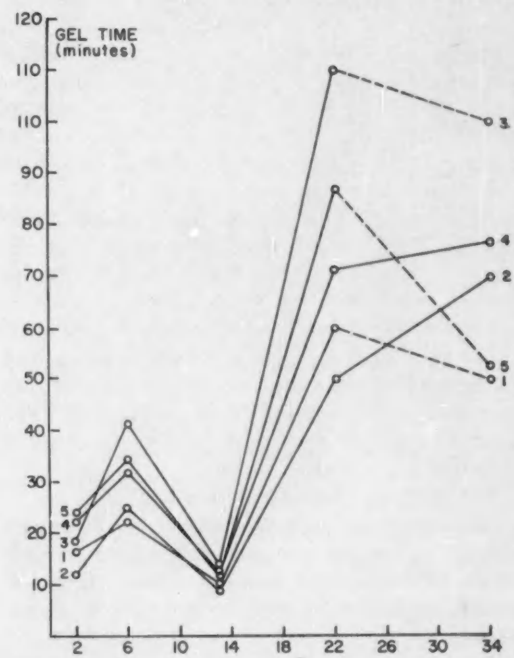

Fig. 3. Gel time as a function of *n* of polyamines (Type II) of formula $[-\underset{|\atop CH_3}{N}(CH_2CH_2O)_nCH_2CH_2-]_x$ in mixture with cross-linking agent $I(CH_2CH_2O)_mCH_2CH_2I$ at a molar ratio 1.6:1 (N:I), 150° C., and pH 10; 25% solids in ethylene glycol. The curves numbered for various values of *m* as in Figure 2.

with the same five cross-linking agents. It is apparent that, in the range studied, the variation of the cross-linking agent has relatively little effect on the gel time, although the differences appear larger when the distance between amino groups is very small or very large. It is equally apparent that, as a first approximation, the gel time increases with increasing distance between nitrogen atoms, except for the striking, consistent, and unexplained minimum which is observed for $n = 13$. The behavior observed raises the question of whether the rate of gelation is a direct function of rate of alkylation or of other complicating factors.

Such a complication might arise from change of the reaction medium as the weight ratio of the reactants changes with their molecular weight. In order to avoid the effect of such a complication, the alkylation of polymers of Type II where $n = 2, 6, 13$, and 22 was carried out with equivalent amounts of a typical cross-linking agent in a more dilute system. The rate of the alkylation reaction was measured by determining the rate at which the halide ions were liberated, and it was found that the intrinsic rate of alkylation decreased regularly with increasing distance between N atoms, without the deviation at $n = 13$ which was observed in the gelation experiments. Figure 4 represents the results obtained in this experiment: the percent reaction is plotted against time at 100° C. for the four reactions investigated. This indicates that minimum gel time observed for $n = 13$ is not due to an anomalous intrinsic reaction rate. Still, we cannot offer a satisfactory explanation for the observations reported.

The effect of varying the frequency of cross-links on the hand of the fabric and on discoloration has been qualitatively investigated for polymers of Type I and II and tentatively correlated to the physical properties of the resins "in bulk."

The following conclusions were reached.

The cross-linked polymer becomes harder as the distance between reactive groups decreases; in other words, as the network becomes tighter. Logically enough, harder resins impart more stiffness to the fabric.

The tendency to discoloration on curing follows the same pattern; it decreases with increasing distance between functional groups. This may be simply the effect of decreased nitrogen concentration.

In view of the significance of gelation for performance, some important questions arise. What percentage of the available functional groups must react before the insoluble three-dimensional network is formed? How does this percentage differ, or does it differ at all for compounds where the frequency of the available cross-linking sites is varied? The following facts were established in an attempt to answer some of these questions.

1. *In vitro*, the alkylation reaction essentially stops when a gel is formed.

2. The alkylation at the gel point (expressed as percent available halide reacted) is independent of the ratio of cross-linking agent to polymer, but the time necessary to reach gelation decreases with increasing ratio of cross-linking agent.

3. With equivalent amounts of the same cross-linking agent, the extent of alkylation at the gel point (as percent available halide reacted) is essentially the same for polymers which differ only in the size of n. For instance, when polymers of Type II were reacted with a cross-linking agent, using 1.6 equivalents of amino nitrogen for each equivalent of halide, analysis of the gels formed for iodide ion gave the results shown in Table I.

TABLE I. Extent of Reaction at Gelling of Polymers $[-N(CH_3)(CH_2CH_2O)_nCH_2CH_2-]_x$ with Dihalide $I(CH_2CH_2O)_{12}CH_2CH_2I$ at Molecular Ratio 1.6:1

n	Gelling time, min.	Iodide groups reacted, %	Amino groups reacted, %
6	41	69	43
13	14	70	44
22	112	74	47

TABLE II. Polymer $[-N(CH_3)(CH_2CH_2O)_{12}CH_2CH_2-]_x$ with Cross-Linking Agent $I(CH_2CH_2O)_{12}CH_2H_2I$ Applied to Dacron (2% add-on)—Cured 3 Min. at 150° C.

Polymer sample	Average molecular weight calculated for polymer	Durability of antistatic finish to laundering[a]
1	5600	30
2	7000	40
3	7000	40
4	7000	35
5	35,000	80
6	35,000	76

[a] Number of launderings required to increase the log of the specific area resistivity to 13.0.

TABLE III. Determination of Branching in Polymers of the Idealized Formula $-[NH(CH_2CH_2O)_{12}CH_2CH_2NHCH_2CH_2NHCH_2CH_2-]_x$

Experiment number	Applied reactant ratio (mols) amine:dichloride	Combined ratio (mols) amine:dichloride	Equivalent weight by amine titration	Equivalent weight from combined ratio	Amino groups, %		
					Primary	Secondary	Tertiary
1	2:1	1:0.89	217	223	28	46	26
2	3:2	1:1.58	367	368	20	50	30
3	3:2	1:1.21	286	290	24	50	26
4	3:2.2	1:1.31	318	312	28	44	28
5	3:2.5	1:1.66	387	382	18	57	25

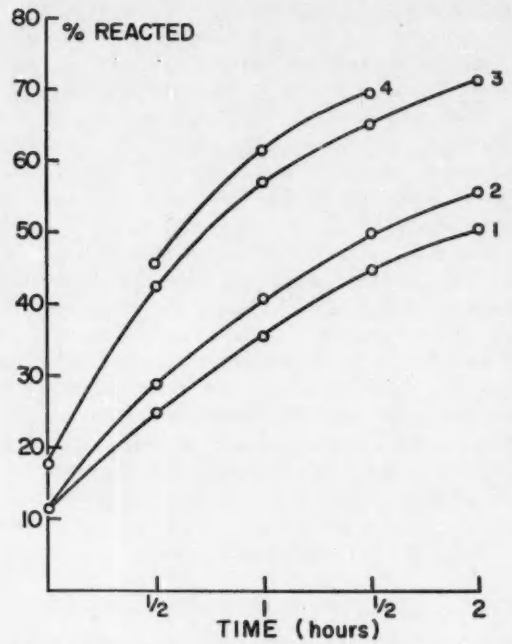

Fig. 4. Rate of alkylation of polyamines (Type II) of formula $[-N(CH_2CH_2O)_nCH_2CH_2-]_x$ with Polyethylene Glycol 600 diiodide. Curve 1: $n = 22$; Curve 2: $n = 13$; Curve 3: $n = 6$; Curve 4: $n = 2$.

Effect of the Degree of Polymerization on Performance

It is expected that soluble polymers of different DP but structurally identical in other respects would form insoluble polymers in the cross-linking reaction at a rate which would increase with increasing DP. The degree of polymerization of the soluble polymers was varied by suitable changes in processing conditions and calculated from the extent of the polycondensation reaction (determined by halide titration), assuming no branching. The results obtained when some of these polymers were applied to fabrics tend to confirm the expectation and are summarized in Table II.

Effect of Branching on Performance

The reaction between amines containing two primary amine groups and dihalides had been first assumed to proceed predominantly to give linear polymers of Type I. The attempt to increase the molecular weight of the polymers without otherwise altering their structure showed, however, that branching was significant and somewhat dependent on the reaction conditions. Table III summarizes the results obtained when the extent of branching was determined in a group of polymers prepared from diethylene triamine and Polyethylene Glycol 600 dichloride.

The conditions employed in obtaining these polymers varied widely, even with respect to the mol ratio of reactants used and to the method of isolation of the polymer for analytical purposes. The second column gives the composition of the reaction mixture. The "combined mol ratio" given in the third column reflects the composition of the reaction product calculated from the amount of residual unreacted diethylene triamine. The differences in the method of preparation explain the lack of correlation between percentage distribution of primary, secondary, and tertiary amino groups on one hand and equivalent weight on the other.

The comparatively high percentage of tertiary amino groups shows that the polymers formed are far from linear; apparently, the reactivity of the primary amino groups is not many times greater than that of the secondary amino groups. On the average, out of four nitrogen atoms, two are linearly linked; the third represents a branching point and the fourth the primary end group. In other words,

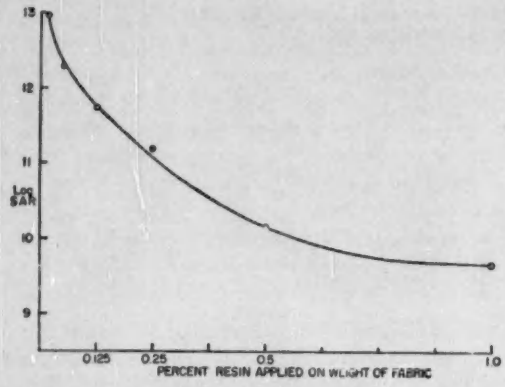

Fig. 5. Log of specific area resistivity in ohms of a Dacron[4] fabric at 30% relative humidity treated with various amounts of polyamine of Type II in mixture with Polyethylene Glycol 600 diiodide and cured.

on the average, each diethylene triamine group contains one branching point. Reduced reactivity of the primary amino groups due to salt formation with the liberated hydrochloric acid might be responsible for the increased mol ratio of the dichloride combined in most of these experiments. In Experiments 2 and 5, the ratio of primary groups drops below that of the tertiary groups, indicating incipient cross-linking (closed branching) in accordance with the increased basic equivalent weight of the polymer. Formation of quaternary ammonium groups was found to be practically negligible in these experiments. Application of the products to fabrics showed that some correlation existed between extent of branching and durability, with branching favoring durability when the products were applied under identical conditions.

By similar analytical techniques, polymers of Type II (at least those with moderate DP) were found to be essentially linear. In this case, branching can occur only by quaternary formation. They remain virtually free of quaternary ammonium groups during the preparation, even though they can be alkylated and cross-linked by employing excess dihalide and/or more severe reaction conditions. In the preparation of the compounds from primary monoamines and dihalides, and subsequent cross-linking, the polyfunctionality of the nitrogen is thus fully exploited. In terms of application to textiles, the specific structure of these polytertiary amines offers certain advantages over polymers of Type I. The concentration of nitrogen in the polymers is the lowest possible for a given dihalide, thus reducing the tendency to discoloration. The nitrogen atoms are free of reactive hydrogens, thus reducing the tendency to discoloration even further. The structure of the polymers and the course of the cross-linking reaction can be more easily controlled, among other reasons, because more meaningful correlations between structure and performance can be established.

Performance of the Resins

In accordance with the principles described here, commercial antistatic finishes were developed based on polyamine resins cross-linked with dihalides. These were found to provide protection against static for all kinds of synthetic fibers and, when applied under suitable conditions, to maintain this protection through a large number of laundering processes (up to 100 launderings and more). The performance data of these products were reported elsewhere [18].

The relation between amount of resin on the fabric and the resulting specific area resistivity is shown in Figure 5. Especially if a large amount of finish is present, the amount of finish and resistivity are approximately proportional, as would be expected when the resin layer acts as a conductor in parallel with the insulating fiber. The breakdown of this proportionality when smaller amounts of resin are present is probably due to lack of continuity in the resin film. Discontinuity would bring the resin in series with the insulating fiber and greatly decrease its contribution to the conductance of the fabric.

The New Principles: Summary

The development reported has produced effective, durable antistatic finishes. More important, the investigation of a new family of polymers has begun and new principles of textile finishing have been successfully applied. The preparation of soluble and insoluble polymers by nitrogen alkylation opens a new chapter for the polymer chemist and for the textile chemist.

It is apparent that the structure and properties of the new polymers can be varied almost at will by a suitable choice of raw materials and that a range of functional properties durable to washing can be imparted to textiles by applying the new finishes.

In addition, the anion exchange properties of the resins, coupled with their outstanding durability, suggest their use as mordants for acid dyes; gen-

erally speaking, the wet resistance of the dyeing is not sufficient for a commercially feasible dyeing method, and the resin retention is not sufficiently high for this purpose. However, modifications of the resin and of the dyeing process (for example, by suitable aftertreatments) gave encouraging results.

The most promising utilization of the resins for dyeing appears to be for pigment binding. The investigation of this application is in progress, and it was shown that dyeing and antistatic finishing can be carried out in one operation. The economic advantages of such a process are obvious.

As the development of new fibers and new fabrics continues, the field of textile finishing becomes a meeting ground for organic chemists, polymer chemists, textile chemists, physical chemists, and physicists. The study of durable antistatic finishes is an example of the integration of principles drawn from many branches of chemistry.

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High Strength Regenerated Cellulose Fibers[1, 2]

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Abstract

Substantial improvements in the physical strength properties of certain fibrous regenerated cellulose products, notably rayon tire cord, have been achieved during the past decade. These advances in tensile and fatigue properties of tire cord rayon are reviewed and the factors responsible for the improvements are discussed in such a manner as to point the way for similar quality gains in related products, such as staple fiber.

Improvement in properties is primarily attributed to the combined use of physical and chemical actions to accomplish controlled crystallite development and orientation in the spinning filament. Beneficial use has been made of various types of chemical regeneration retarding agents to prolong the plastic–gel state, thereby facilitating heavy stretching along with dehydration of the coagulated filament to yield a highly consolidated and uniaxially oriented structure prior to complete regeneration.

The relation of current spinning practices to mechanical properties attained in the final filament are outlined and interpreted in the light of filament cross-sectional structure, secondary swelling properties, and differential dyeing characteristics.

Potential strength aims for future cellulosics are discussed and some suggestions made as to the type of products for which the structural skeleton of the cellulose polymer appears to offer outstanding advantages, particularly when coupled with bonding or stabilizing resins in intimate molecular association.

THE LAST few years have brought substantial improvements in the physical strength properties of certain regenerated cellulose fibrous products, notably the type of high strength rayon yarn used for tire cord. This trend has been so striking as to reach the point where the present-day high strength rayon is an entirely different fiber from the product known only five to ten years ago. This is especially true for the advanced fibers now in the development stage. Unfortunately, some segments of the rayon industry have been rather slow in completely utilizing the technology whereby these advances have been made; consequently most of the fibrous rayon products available today to the end-product consumer are still deficient in many respects.

In order to stimulate progress in production and utilization of top quality products, it is desirable that the means whereby the pioneering advances have been made be considered. This will afford some insight into the relation between structure and mechanical behavior of regenerated cellulose fibers and should point out the important factors that need be practiced in order to realize commercial scale improvements in the quality of rayon end-products.

The steady incremental improvements that have already been achieved in recent years in the physical properties of tire yarn are shown graphically in Figures 1, 2, and 3. Figure 1 depicts the change in the tensile properties of high tenacity rayon yarn as exemplified by the strength in grams per denier of the oven-dry, conditioned, and wet fibers. Moreover, it will be noted that an even more marked change has occurred in the rate of improvement in fatigue life potential, as shown in Figure 2. Here the upward trend is quite pronounced and is still continuing unabated.

Accompanying progress in improved tensile strength and fatigue resistance of rayon yarn has been a decrease in the wet swelling characteristics, as illustrated in Figure 3. The projected data here suggest that rayon can eventually be made fully equivalent to cotton in its secondary swelling be-

[1] Presented before the Division of Cellulose Chemistry, 132nd A.C.S. Meeting, New York, N. Y., September 8–13, 1957.

[2] Contribution No. 34 from the Research Division of Rayonier Incorporated.

havior, and likely in its wet strength and ability to withstand laundering. To attain full launderability and dimensional stability, it may be necessary to supplement the oriented and crystallized regenerated structure by "built-in" stabilizing resins or structural cross-links. Knowledge in this field is also advancing rapidly.

A close look at the physical properties depicted in these curves rather clearly indicates that the most significant developments have occurred in recent years, and particularly within the last four years. This has been primarily due to the advent of "super" spinning technology based on modifications of the regeneration behavior of cellulose to slow xanthate decomposition and permit effective application of a high degree of orienting stretch prior to complete regeneration. Many interrelated factors are involved, however, and they should be considered in conjunction with one another in proper relation and balance.

Perhaps the most important factor leading to development of the improved technology is the recognition that certain chemicals added to viscose serve to stabilize xanthate decomposition, thereby prolonging the period when effective stretch may be applied. Coupled with use of high salt index, high zinc, and high temperature dehydrating types of spinning baths, the viscose "regeneration retardants" or "modifiers" become very flexible tools for development of "short-span" crystalline alignment. They are added to the viscose prior to the spinning operation and increase the period in which the extruded filament is in a plastic–gel state between coagulation and regeneration. While hundreds of chemical compounds have capabilities to act as viscose retardants, the most widely known fall into the five general chemical classes illustrated in Table I.

The low molecular weight aliphatic amines [2] and the quaternary ammonium salts [3] were the chemical classes originally suggested for use as viscose modifiers. Although many specific aliphatic amines have been mentioned in the patent literature as being suitable, cyclohexylamine is typical of this type of modifier. Trimethylbenzylammonium hydroxide is typical of the quaternary ammonium salt. Shortly after the advent of the nitrogen-base regeneration retardants, it was discovered that polyoxyalkylene derivatives also function in a similar capacity [10]. In this chemical class a great deal of variety is possible, involving not only different oxyalkylene constituents of varying lengths and arrangements but also polyoxyalkylene derivatives involving various types of end groups and base molecules. Simple poly(ethylene oxide) and block copolymers of poly(ethylene oxide) and poly(propylene oxide) are low in cost and quite effective. This class has been greatly expanded by the condensation of ethylene oxide with all types of base molecules. The polyhydroxy polyamines, as typified by N,N,N′,N′-tetrahydroxyethyl-1,3-diamino-2-propanol, combine the functional groupings of the amine type and the

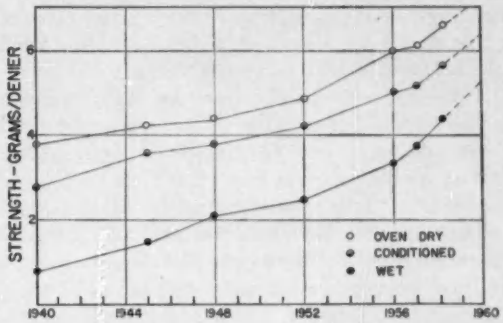


Fig. 1. Tensile properties of high strength rayon yarn.

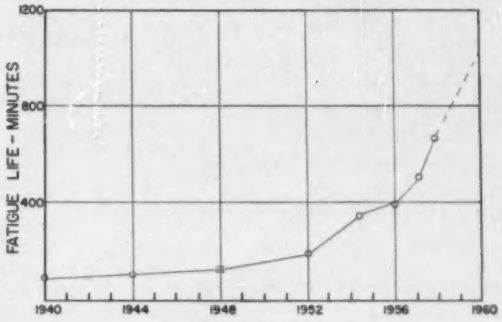


Fig. 2. Fatigue life of high strength rayon.

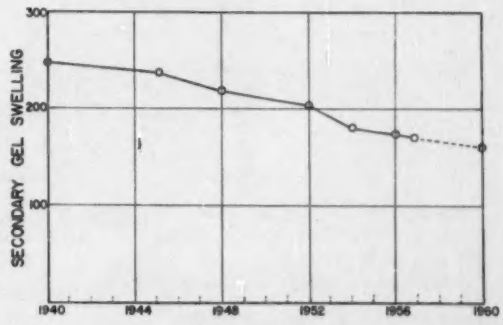


Fig. 3. Wet swelling of high strength rayon.

polyoxyalkylene type [9]. Another chemical class that is also related to the aliphatic amine compounds consists of the sodium salt of low molecular weight dithiocarbamates [5]. The variety of chemical groupings noted in the aliphatic amine type is also present in the dithiocarbamate series.

Many other viscose chemical "modifiers" have been proposed which combine the various features and functional groupings of the compounds described above in varying proportions and through assorted chemical linkages. These, however, appear to function largely due to the presence of the active chemical grouping already described rather than as a result of a unique chemical combination.

While the use of a viscose regeneration retardant is characteristic of the "super" spinning processes, it is not sufficient of itself to give oriented high strength in the so-called all-skin filaments. The presence of the retardant does appear to promote various physical and chemical conditions, but unless advantage is taken of these conditions no real improvement is realized during the spinning operation. This is illustrated in Table II, which shows a summary of processing conditions used for various successively improved spinning processes. It will be noted that in going from the regular type viscose spinning process to the most advanced "improved-super" type that, in general, an increase in the zinc content of the spinning bath is involved as well as an increased salt index level of the viscose to be spun along with increased application of multi-stage stretching. To investigate the whole range of these variables properly requires extreme flexibility in all stages of spinning and processing. An experimental spinning machine that has been specifically designed to provide an extremely wide latitude in stretch ranges along with precise operating control is shown in Figure 4.

The older regular spinning technique in commercial use ten years ago involved an acid bath composition of generally less than 4% zinc sulfate and a salt index at spin of about 4 to 6 maturity, with stretching in the range of 60–70%; no modifier was used. In the super and improved super processes in use today, however, modifier is employed in both the viscose and the primary spin bath along with a comparatively high zinc content. A secondary low

TABLE I. Typical Viscose Regeneration Retardants

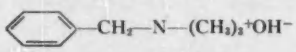
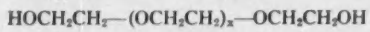
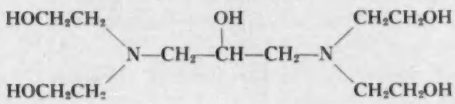
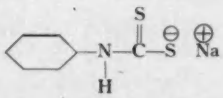
Chemical type	Example
Aliphatic amine	
Quaternary ammonium salt	
Polyoxyalkylene derivative	
Polyhydroxy polyamines	
Dithiocarbamate	

TABLE II. Summary of Viscose Spinning Conditions

Process	Modifier	Acid bath, %			Salt index	Stretching, %	Conditioned tenacity, g./den. (1650/2, 11.5×10.5)	Fatigue life, min.
		$ZnSO_4$	H_2SO_4	Na_2SO_4				
Regular	None	1–3	7–10	18–23	4.0– 6.0	50–70	2.5–2.8	100
Intermediate	None	3–7	7–10	18–23	4.0– 9.0	60–90	2.8–3.2	200
Super	In viscose and bath	4–9	7–10	18–23	6.0–15.0	80–120	3.2–3.6	300
Improved super	In viscose and bath	4–9	7–10	18–23	6.0–15.0	80–150	3.8–4.2	600
Experimental	In viscose and bath	6–10	7–9	12–18	10–15	100–200	4.2–5.0	1000

acid, high temperature bath has been introduced and the viscose is spun at a higher maturity level; considerably increased stretching is also employed. This necessitates great care or "coddling" of tender filaments involving use of bath-fed "tubes" [4], extrusion at lower speeds, and more gradual application of stretch.

In a complex process such as the spinning of viscose, a variety of interrelated physical and chemical effects are operative. The chemical reactions occurring during the spinning of viscose can best be considered as outlined in Figure 5, where only the pertinent reactions are shown. The viscose-making process converts the cellulose raw material into the alkali-soluble sodium cellulose xanthate. Upon extrusion into the acid bath, this salt is converted into the cellulose xanthic acid, which very rapidly decomposes into regenerated cellulose. In this normal acid regeneration sequence the reactions occur very rapidly, and little opportunity is available for stretching the filament to induce orientation. In the presence of zinc, however, there is some conversion of the sodium cellulose xanthate into the corresponding zinc salt. The zinc cellulose xanthate is considerably more stable in an acid medium than is the sodium salt; consequently, the conversion of the zinc cellulose xanthate into the xanthic acid is much slower because of the requirement for greater diffusion of acid ion into the interior of the filament. The overall regeneration of the cellulose from a viscose solution in a zinc-containing acid bath is then a more gradual conversion. This slower regeneration provides more time for stretching and orientation.

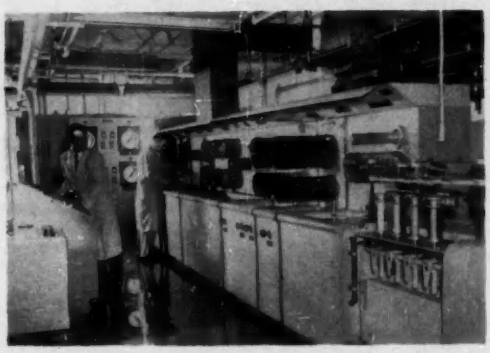


Fig. 4. Experimental continuous spinning machine.

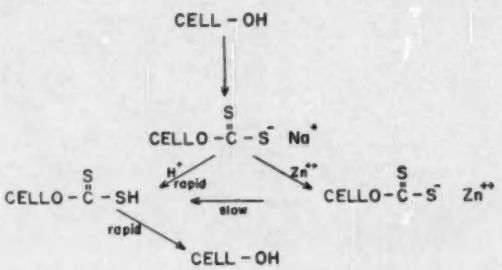


Fig. 5. Viscose reaction sequence.

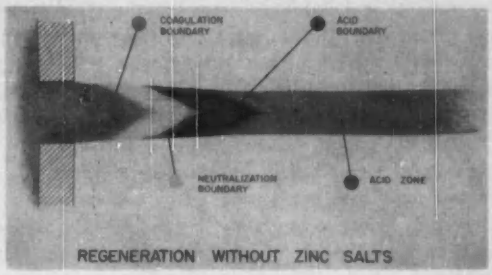


Fig. 6. Schematic representation of viscose spinning into an acid bath without zinc salts.

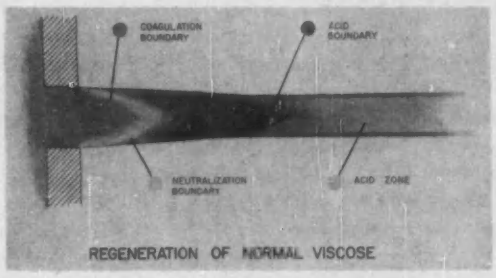


Fig. 7. Schematic representation of viscose spinning into a normal bath. Skin area noticeable on filament surface at right side of photograph denotes zone having gone through zinc xanthate stage.

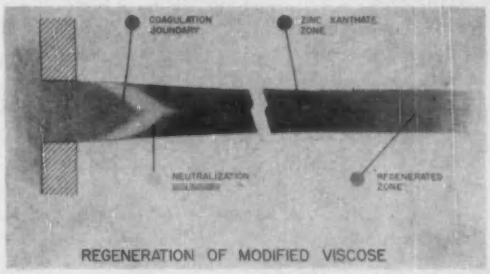


Fig. 8. Schematic representation of "modified" viscose spinning. Break in filament in plastic-gel area may extend for distance of few inches or with certain good retardants up to several feet.

These idealized reactions can be visualized as occurring within rather lengthy and diffuse boundary areas in the spinning filament. The situation existing [7] in a viscose filament extruded into a spin bath containing only sodium sulfate is illustrated schematically in Figure 6. The viscose being extruded through the spinnerette orifice into sulfuric acid is coagulated by the action of the hot astringent spin bath into a gel. Penetration of the acid into this gel filament is gradual, resulting in a diffused neutralization boundary. As additional hydrogen ion enters into the filament, the gelled xanthate zone is replaced by an acid zone wherein the cellulose has been completely regenerated. These changes occur in rather rapid sequence in the absence of zinc salts in the bath.

Figure 7 depicts the regeneration of viscose in a normal type bath containing a low concentration of zinc salt. Here coagulation occurs rapidly, as before, and penetration of the acid results in the neutralization zone. However, in addition to the penetration of the acid, the zinc ions from the spin bath also penetrate the filament, seemingly to precede the initial hydrogen ions, which are neutralized by the caustic. This results in some conversion of sodium cellulose xanthate into zinc cellulose xanthate. Such conversion, however, is primarily restricted to the outer portion of the filament inasmuch as the acid is able rather quickly to overtake the scant zinc content and penetrate into the filament in a concentration sufficient to accomplish relatively rapid regeneration. Consequently, the cellulose on the skin of the filament has undergone slightly different physical and chemical transformation than the bulk of the cellulose in the interior of the filament due to partial zinc xanthate formation [8].

Figure 8 illustrates the regeneration of a viscose containing a regeneration retardant in the presence of a high-zinc spin bath. As before, coagulation and the initial neutralization boundaries are established; however, in this case the presence of the regeneration retardant markedly affects the comparative penetration rates of the zinc and the acid components of the spin bath. Zinc cellulose xanthate formation is much more extensive and can actually occur throughout the entire filament ahead of acid in regenerating concentration. Because the decomposition of the zinc cellulose xanthate is considerably slower than that of the sodium xanthate, the overall regeneration is markedly decelerated, and a fairly discrete zinc xanthate zone is established. The action of the retardant is in effect that of a selective sieve permitting passage of zinc ahead of acid. The retarding of the overall cellulose regeneration process results in the spinning filament being in a "green," highly plastic, and stretchable state for a considerably longer period of time than in the normal-type spinning process. This situation allows for a more extensive stretching to be applied to the filament and insures that the filament is in a condition such that it will accept the stretch more effectively. The overall result of the presence of the regeneration retardant in the viscose along with the higher zinc concentration of the spinning bath is the more complete conversion of the sodium cellulose xanthate to zinc cellulose xanthate prior to penetration of acid. This permits more effective multi-stage elongation, dehydration, consolidation, and orientation and the formation of smaller crystallites, as well as other changes in the spun fiber.

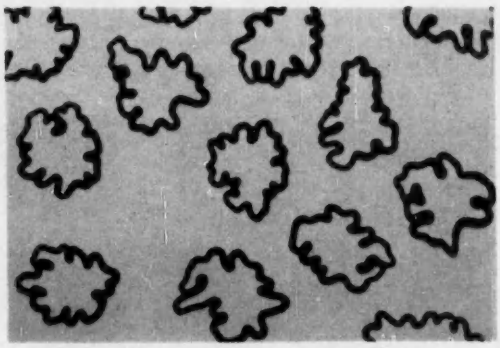


Fig. 9. Dyed cross-sectional photomicrograph of regular type viscose rayon.

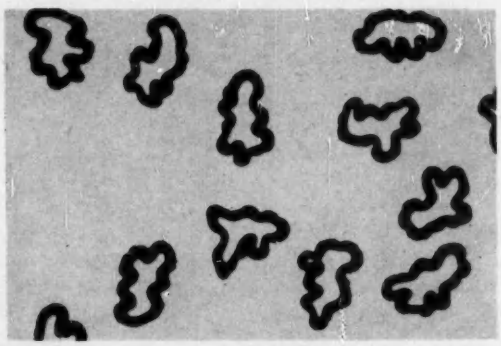


Fig. 10. Dyed cross-sectional photomicrograph of intermediate type viscose rayon.

One of the readily apparent differences in the super-type yarns spun from modified viscose over that of the regular viscose yarn may be observed in the differentially dyed [11] filament cross section, also in phase contrast [1]. Figure 9 illustrates the dyed cross section of a regular type viscose rayon; it is typical of the skin-core relationship existing in this type of product [8]. The exterior skin is considered to be composed of that cellulose which has gone through the zinc cellulose xanthate form. The skin is comparatively thin, and the overall filament outline is quite irregular, showing high shrinkage and lack of dehydrating consolidation while in the plastic–gel state. Both conditions are typical of the older regular-type yarn in production several years ago, or of textile-type rayons.

Figure 10 illustrates a dyed cross section typical of an intermediate-type rayon fiber. Here the cross section is less crenulated in shape, and the filament contains a considerably thicker skin. In addition, the skin contains a number of small black spots which are small voids within the skin structure. In the super type spinning process, the more complete conversion of the sodium cellulose xanthate to the zinc salt occurs; consequently, the dyed cross section shows an all-skin structure, as illustrated in Figure 11. Further, the filament outline has become more rounded and the small voids are completely distributed throughout the structure. The voids are thought to result from gas developed in xanthate decomposition occurring substantially after stable gel formation.

Figure 12 illustrates another dyed yarn cross section which is again rather typical of certain modified viscose spinning systems. This sample has an all-skin structure, but the filament has the elongated dog-bone shape instead of a circular form. Several variations of the all-skin yarn are possible, depending upon the type of modifier employed and the physical and chemical conditions encountered during spinning. The changes observed in the differentially dyed cross section of viscose filaments in going from

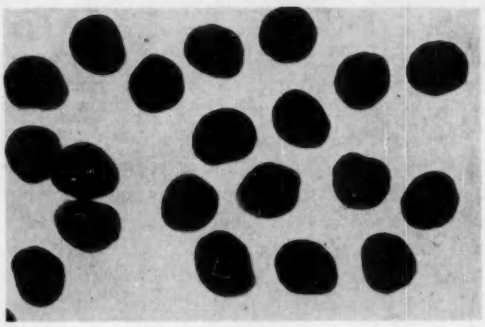


Fig. 11. Dyed cross-sectional photomicrograph of "all skin" super type viscose rayon.

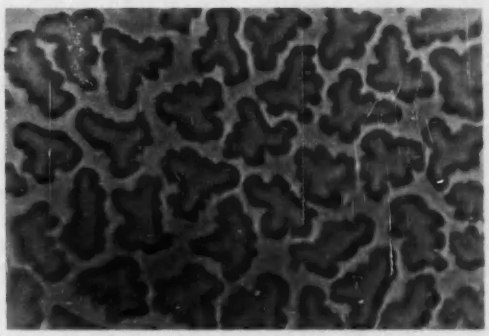


Fig. 13. Phase cross-sectional photomicrograph of normal type viscose rayon.

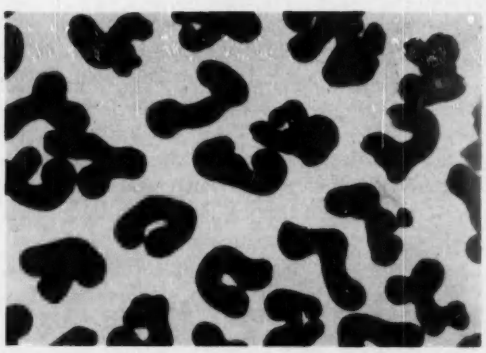


Fig. 12. Dyed cross-sectional photomicrograph of another super type viscose rayon.

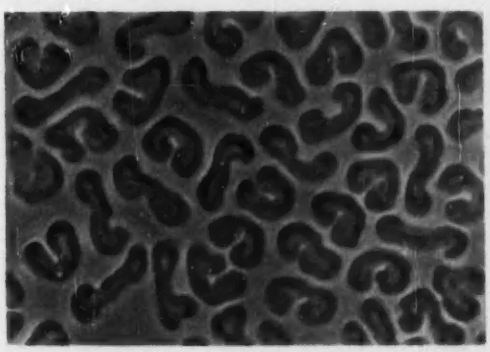


Fig. 14. Phase cross-sectional photomicrograph of an intermediate type viscose rayon.

the normal to the super type spinning process are also noted in phase cross sections [1]. Figure 13 illustrates the phase cross section of a normal type viscose rayon. The irregular filament outline shown in the dyed section is still apparent, while the cross-sectional structure is comparatively free from characteristic voids. The phase cross section of an intermediate type is shown in Figure 14.

Figures 15 and 16 illustrate phase cross sections of super type yarns. As noted in the dyed section, the outline of the filament is quite uniform and regular, and voids are uniformly distributed throughout the filament.

Although considerable study has been devoted to the voids occurring within the super type filaments, at the present time they are considered to be a structural feature resulting from the chemical and physical conditions occurring within the filament at the time of spinning. They, of themselves, are not considered to convey strength to the super-quality products, but rather denote a condition that exists during the latter phase of the regeneration sequence and probably result from decomposition to gaseous products that has occurred after establishment of a rather discrete gel structure substantially prior to complete regeneration.

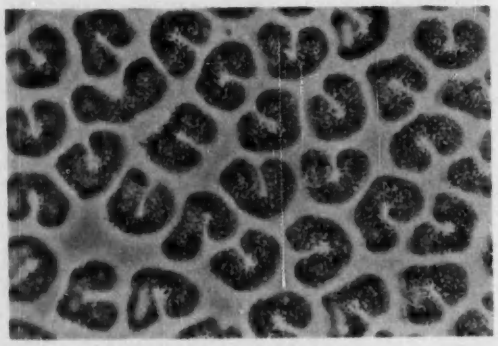


Fig. 15. Phase cross-sectional photomicrograph of super type viscose rayon.

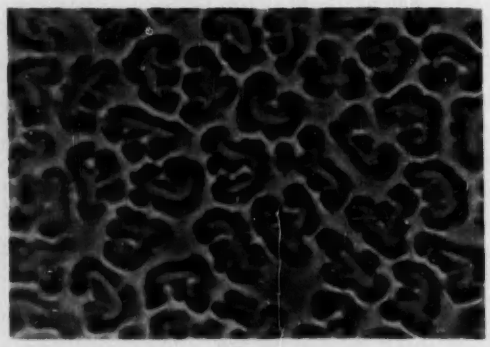


Fig. 16. Phase cross-sectional photomicrograph of another super type viscose rayon.

The material added to the viscose to effect the retardation of regeneration processes are of vital importance in the spinning operation, particularly as they affect runability, stretchability, cratering, speed of production, shape of filament, etc. Consequently, considerable interest has existed in chemical structures which can effect retardancy as well as speculation as to the mechanisms whereby the action is achieved. Although this is a research area in which considerable work is being done, a complete and satisfactory theory to explain observations on retardancy capabilities is not yet available; however, it may be instructive to consider some of the chemical mechanisms that have been suggested to explain the action of the various chemical classes of regeneration retardants. Although none of these theories is completely satisfactory in every detail, some do provide a background for predicting the effect of various spinning variables on the super spinning process and may provide a base for consideration of further work.

One explanation that has been proposed to account for the action of nitrogen-containing compounds during the viscose spinning operation is based on the formation of a labile complex between the zinc, the amine compound, and sodium trithiocarbonate. It has been suggested that this complex facilitates the penetration of the zinc ion into the spinning filament by solubilizing the zinc over a wide pH range, thus allowing the zinc to traverse the pH barrier existing between the highly alkaline interior and highly acidic exterior. The zinc within the solubilized complex can penetrate into the interior of the filament ahead of the neutralization boundary and thus be available for reaction with the sodium cellulose xanthate at the appropriate pH prior to the entrance of the acid, which would rapidly decompose the sodium derivative. Another theory proposed to explain the action of aliphatic amines is based on the conversion of the amine to the corresponding sodium dithiocarbamate through the action of the excess CS_2 contained within the viscose solution:

$$R{-}NH_2 + CS_2 + NaOH \longrightarrow R{-}NH{-}\overset{\overset{S}{\|}}{C}{-}S{-}Na + H_2O$$

This chemical reaction is comparatively rapid, and ample opportunity is available for such a conversion to occur during the ripening stage of the viscose process. During spinning, the dithiocarbamate salt existing within the filament could conceivably react with the incoming zinc ions forming the zinc dithiocarbamate salt. This salt, being only slightly soluble in water, could function as a mechanical barrier to the rapid migration of acid into the filament. As the acid concentration increased, however, the barriers would gradually decompose at the low pH and then permit the acid to progressively migrate into the interior of the filament. This would occur after the zinc has penetrated and formed the zinc cellulose xanthate. Each of these mechanisms serves to explain many facts that have been observed in studying regeneration of modified viscose; however, neither is completely perfect in providing all the answers. It may be possible that both mechanisms are operative and certain compounds function by a combination of the two mechanisms, whereas with other compounds one mechanism may predominate.

Compounds based on polyethylene glycol obviously cannot function by the same mechanism proposed for nitrogen-containing modifiers. One mechanism proposed for this class of chemical compounds is based upon the basicity of the oxygen in the ether linkage. It is well known that a normal ether oxygen atom is comparatively basic; dimethylether actually forms a salt-like derivative with hydrogen chloride:

$$CH_3—O—CH_3 + HCl \longrightarrow [CH_3—\overset{H}{O}—CH_3]^+ + Cl^-$$

Further, it has been shown by a number of investigators that polyoxyethylene derivatives in water combine with one water molecule per ether linkage [6]. It has been suggested that the polyoxyalkylene compounds function as regeneration retardants by providing an alkaline reserve in the long polyether chain through formation of a polyoxonium salt:

$$—R—O—R—O—R—O—R—O—R—O— + H^+ \longrightarrow —R—O—R—O—R—\overset{H^+}{O}—R—$$

While such a salt would be comparatively labile, it could function to retard the migration of hydrogen ions into the spinning filament and permit the zinc to precede the acid and allow formation of the zinc cellulose xanthate. This mechanism for the action of retardancy is probably oversimplified, inasmuch as not all polyoxyalkylene compounds are effective. However, this mechanism, coupled with other basic requirements such as solubility, upper and lower DP limits, hydrophilic–hydrophobic balance, and absence of interfering groups, permits the prediction of retardancy action in a considerable number of compounds.

Compounds of the polyhydroxy-polyamine type may function by a combination of the mechanisms described or be predominately one or the other, depending upon the dominance of the amino group versus the oxygen function.

In considering the basic end-product requirements for the various applications of viscose rayon fibers, several interrelated characteristics are required. Most of these requirements can be met, however, by a balanced combination of variables available to the viscose fiber technologist.

The production of a truly launderable rayon staple is one area in which the utilization of these principles will no doubt find increasing application. In this field the principal future end-product requirements will include superior wet strength, increased resistance to fibrillation and abrasion, improved dimensional stability, and increased resistance to chemical degradation. These requirements, of course, should be met without any loss in the desirable properties of cellulosic fibers: good moisture absorbency, dyeing qualities, etc. It is noteworthy that "super" spinning techniques should provide a means of achieving these objectives. Improved wet strength and lowered swelling characteristics are already obtainable by this means. Both of these features should lead to greater dimensional stability. As orientation is increased by the greater stretching, these properties should improve also. Fibrillation should be inhibited by development of smaller crystallite size. An indication of the potential properties for such a launderable type staple compared to the

TABLE III. Summary of Viscose Rayon Staple Single Filament Data

	Regular	Intermediate	Super
Den./fil.	1.50	1.50	1.50
Tenacity, g./den.			
Conditioned	2.80	3.65	4.50
Wet	1.50	2.75	3.75
Elongation, %			
Conditioned	22.0	20.0	20.0
Wet	28.0	26.0	24.0
Secondary swelling	210	190	170

present normal product is shown in Table III. These single filament data show that real improvements are obtainable in all the single filament physical properties. To achieve complete launderability, however, it will probably still be necessary to employ a resin stabilization treatment. Considerable stabilization can likely be achieved, however, by incorporating a cross-linking resin with the modified viscose. Present indications are that this approach is very realistic and portend rapid developments in this direction.

While a considerable body of technology now exists for the production of viscose fibers, based on "super" spinning practices, more widespread understanding and application of these principles will be required before their full potential is realized.

By judicious application of the facts already known as a starting point and through the wide range and versatility afforded by the multitude of chemical types available as regeneration retardants, considerably greater strides should be possible in the future.

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INDUSTRIAL SECTION

Amine Odor in Resin-Treated Fabrics[1]

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Introduction

One of the problems associated with the use of nitrogenous resins on textile fabrics is the spasmodic and usually unpredictable development of fishy amine odor. Sometimes this is noticed during curing, but more often it becomes evident during storage or use of the treated fabrics. The incidence of odor is not high, considering the large quantities of fabrics that are resin treated, but the odor is so universally regarded as unpleasant that, when it occurs, it nearly always leads to a complaint. The situation is made worse by the fact that most such complaints are concentrated within a few hot, humid months, sometimes giving the appearance of an epidemic.

Undoubtedly, much study has been made of the amine odor problem, both in the mills and among chemical companies. For the most part, however, the results have not been published. A noteworthy exception is the excellent study by Fluck and coworkers [1], which in some respects served as a point of departure for the present investigation.

The original purpose of the present study was to determine the relative importance of four chemicals that had been reputed to have some influence on odor development: (a) ammonia and (b) formaldehyde, which have long been thought to interact to produce trimethylamine, the fish-smelling substance [7]; (c) traces of copper, which had been found by Gruntfest et al. to catalyze fish odor when a urea-formaldehyde paste resin was heated to 400° F. [3]; and (d) sodium formate, mentioned by Fluck at al. as enhancing fish odor development when present in padding baths [1].

Later, the investigation was extended to cover other phases of the problem. The results of the study will be reported in three sections: factors influencing trimethylamine formation, the effect of type and concentration of catalyst, and the effect of type of resin. For better continuity, certain of the experimental details and much of the theoretical discussion will be relegated to the Appendix.

Factors Influencing Trimethylamine Formation

In the first experiment, a urea-formaldehyde (UF) paste resin[3] was dissolved in water to give a 15% solids solution. This was deionized (and thereby freed of ammonium, formate, and copper ions) by passing it through a layer of Amberlite XE-81, a mixed bed ion-exchange resin capable of removing both cations and anions. Then (a) where ammonium ions were to be present in the padding bath, 0.5% diammonium phosphate was added as catalyst; where ammonia was to be absent, 0.1% tartaric acid was substituted. Formaldehyde was assumed to be present in sufficient quantity from the UF resin; (b) where the concentration was to be as close to zero as possible, 1% urea was added as a formaldehyde acceptor (as suggested by Fluck et al.). Finally, (c) 0.1% cupric acetate and (d) 0.5% sodium formate were added where those ions were to be present. These methods of controlling the presence or absence of the four ingredients are summarized in Table I.

[1] Presented at the Chemical Finishing Conference of the National Cotton Council, Washington, D. C., October, 1958.

[2] Mr. Olney, at present with Atlas Powder Company, Wilmington, Delaware, contributed to the first section of the work.

[3] Although etymologically incorrect, the term resin will be used throughout as a convenient synonym for resin-forming precondensate or reactant, in accord with mill practice.

Sixteen resin baths were made up, each containing 14% solids of a UF paste resin precondensate and small amounts of the variables under test, in all possible combinations. These baths were applied to rayon challis by dipping, squeezing (100% pickup), air drying at 80° F., and curing 10 min. at 300° F. The fabrics were not afterwashed.

To test for odor, the Kraus procedure was used [4]. This involves boiling the fabric sample in water and distilling the TMA (trimethylamine) over into a solution of iodine in potassium iodide. A dark brown precipitate, probably trimethylamine tetraiodide, is a positive result. For a more complete description of the test, see the Appendix. While we have not had enough experience with this procedure to consider it completely reliable under all circumstances, we have much more confidence in it than in the vagaries of the "nose" test, even when a panel of observers is used.

TABLE I. Methods of Controlling Presence or Absence of Various Components

	To be Present	To be Absent
Formaldehyde	Present in resin	Add urea
Ammonia	Added as $(NH_4)_2HPO_4$ catalyst	Deionize; use tartaric acid catalyst
Copper	Added as $Cu(OAc)_2$	Deionize
Formate	Added as HCOONa	Deionize

In any event, the Kraus procedure gave unequivocal results—definitely positive or negative—throughout most of our work. This was particularly true in the earlier experiments, where relatively large amounts of potential odor-forming materials were purposely added.

The results (see Table II) were as astonishing as they were clear-cut: *only those combinations containing formate ion produced TMA, but those always did, even where no free NH_4 or CH_2O was originally present.* Formate is obviously an essential component in the TMA reaction under the conditions encountered here.

On the other hand, we cannot conclude that ammonia and formaldehyde play no part in TMA formation. Instead, we must infer that (a) ammonia in sufficient quantity can be produced by breakdown of the urea of the UF resin, and (b) urea added as a formaldehyde acceptor is not efficient enough to prevent TMA formation where other conditions are favorable.

Copper does not seem to take an essential part in the reaction. The fact that it has been shown to exert a catalytic effect (at temperatures higher than those used here) may be due to its ability to assist the oxidation of formaldehyde to formic acid. This possibility will be referred to later.

TABLE II. Effect on TMA Formation of Various Components Added to Urea-Formaldehyde Padding Solutions

Sample no.	Free CH_2O	0.5% $(NH_4)_2HPO_4$	0.1% $Cu(OAc)_2$	0.5% HCOONa	Kraus test*
II-1	—	—	—	—	0
2	X	—	—	—	0
3	—	X	—	—	0
4	—	—	X	—	0
5	—	—	—	X	+++
6	X	X	—	—	0
7	X	—	X	—	0
8	X	—	—	X	+++
9	—	X	X	—	0
10	—	X	—	X	+++
11	—	—	X	X	+++
12	X	X	X	—	0
13	X	X	—	X	+++
14	X	—	X	X	+++
15	—	X	X	X	+++
16	X	X	X	X	+++

* Scale: +++, copious precipitate; 0, none.

To confirm the tentative hypothesis that sources of ammonia, formaldehyde, and formate must all be present to form TMA, the experiments listed in Table III were run. Applications were made to rayon challis as before, curing 10 min. at 300° F.

It is evident that, under the conditions of the experiment, sources of NH_3, CH_2O, and formate must all be present; otherwise no TMA will be produced. Trial III-6 shows that urea can serve as the source of NH_3, while III-7 shows that the UF resin can serve as the source of both NH_3 and CH_2O.

It has not been previously recognized that in some instances three components are required for TMA formation. Fluck et al. mention repeatedly that formate intensifies fish odor and so should be avoided, but none of the several possible reaction mechanisms they cite (see Appendix) shows formate as an original component. Yet we can state as a general rule that, in the case of the paste UF resin such as employed here, formate is an essential ingredient.

Effect of Heat and Acidity

On theoretical grounds, we might suppose that the reaction of ammonia, formaldehyde, and formate would be encouraged by heat and acidity. The effect of heat is shown in Table IV. Several conclusions are readily apparent. The more severe the cure, the more TMA is produced. This confirms the findings of other investigators [1, 7]. On the other hand, it must be recognized that *when ample formaldehyde, ammonia, and formate are present,* very moderate curing conditions will produce TMA. The effect of longer periods of time (days or weeks) at lower temperatures has not been studied sufficiently to warrant the drawing of conclusions.

The need for acidity is somewhat less apparent. There is ample evidence that very moderate acidity, even less than that normally used for catalysis of thermosetting resins, is sufficient to catalyze TMA formation. Moreover, in some instances TMA will form under mildly alkaline conditions—as, for example, from formaldehyde, sodium formate, and ammonium carbonate (see Table III). On the other hand, TMA is less likely to form when the fabric is definitely alkaline, as shown in Table V. (Alternately, we might conclude that if any TMA is formed under alkaline conditions, it immediately volatilizes. This matter has not been further studied.)

TABLE III. Components Involved in TMA Formation

No.	UF resin	CH_2O*	NH_4	HCOONa	Kraus test
III-1	None	1%	1% NH_4Cl	1%	++
2	None	1%	1% NH_4Cl	—	0
3	None	1%	—	1%	0
4	None	—	1% NH_4Cl	1%	0
5	None	1%	1% $(NH_4)_2CO_3$	1%	++
6	None	1%	5% Urea	1%	++
7	12% Solids	**	**	1%	++

* 37%, deionized.
** Evolved from UF resin. In this trial 0.2% tartaric acid added as catalyst.

TABLE IV. Effect of Curing Conditions on TMA Formation

Conditions: 12% solids UF resin, 0.5% diammonium phosphate catalyst, 0.5% sodium formate

No.	Curing time, min.	Temp., °F.	Kraus test
IV-1	5	200	0
2	30	200	0
3	3	240	0
4	4	240	0
5	5	240	+
6	1	300	++
7	60	300	+++

Scale: 0, no TMA; +, slight ppt.; ++, moderate; +++, copious.

TABLE V. Effect of Acidic vs. Basic Catalysis

Conditions: 12% solids UF resin, 0.25% sodium formate

No.	Catalyst	Cure	Kraus test
V-1	0.5% diammonium phosphate	10 min. 300°	++
2	0.5% amine hydrochloride	10 min. 300°	++
3	0.1% tartaric acid	10 min. 300°	++
4	0.5% sodium bicarbonate	10 min. 300°	0
5	2.0% sodium bicarbonate	10 min. 300°	0
6	2.0% sodium bicarbonate	30 min. 300°	0

Effect of Formate Concentration

Further study has shown that there is a lower limit below which (other conditions being fixed) the presence of formate does not result in noticeable fish odor. In addition, a comparison has been made between Kraus test results and results of a "test panel" who smelled the fish odor evolved when the fabric was wet with warm (120° F.) dilute soda ash solution.

Table VI lists the results of a study of sodium formate concentration. The padding bath contained

15% solids UF paste (this provides CH_2O) and 0.5% diammonium phosphate catalyst (source of NH_3), applied to rayon as before and cured 10 min. at 300° F. In the subjective "nose" test the ratings were made by five observers, using the scale N (none), F (faint), S (strong).

Some of the F (faint) ratings must be discounted because two of the observers believed they smelled fish odor in the water control, which contained no resin, catalyst, or formate. Nevertheless the overall correlation is gratifying. About 0.1% formate is necessary to obtain a positive Kraus test, while the nose is probably more sensitive as well as more erratic.

A similar study, made with formic acid, showed that the threshold is between 0.2 and 0.5%. Part of the acid apparently volatilized during the drying at 80° F. preceding the cure. No comparative study was made of high temperature drying, as would occur in mill application.

TABLE VI. Effect of Sodium Formate Concentration

Conditions: 15% solids UF resin plus 0.5% $(NH_4)_2HPO_4$

No.	HCOONa	Kraus test	Subjective fish odor*				
			A	B	C	D	E
VI-1	0.005%	0	N	N	N	F	N
2	0.01	0	N	N	F	F	N
3	0.05	0	F	F	F	N	F
4	0.10	+	F	S	S	F	F
5	0.50	+++	S	S	S	S	S
6	Water control	0	N	N	F	N	F

* Scale: N, none; F, faint; S, strong.

The Role of the Formate

A more fundamental question concerned the part that formate plays in the production of TMA—how does it operate, and is its action unique? Especially, is there any way to circumvent its action?

While it did not seem likely that the carboxyl group was in any way responsible, a few other acids and salts were tried, with negative results. For example, acetic acid, which is adjacent to formic in the fatty acid series, was ineffective. So were tartaric and oxalic acids.

From general considerations (see theoretical discussion in the Appendix) it seemed likely that the formate ion was acting as a reducing agent. Yet other reducing agents, substituted for it, did not produce TMA (Table VII, Trials 1–5). It is quite possible that formates are unique in this application, although the reason for this is not clear.

Attempts to circumvent the action of the formate have not been successful. For example, the addition of a second reducing agent to baths containing formate, in the vague hope of "confusing" the course of the reaction so that no TMA would be produced, was not effective (Table VII, Trials 6–8).

TABLE VII. Effect of Oxidizing and Reducing Agents Added to Urea-Formaldehyde Pad Liquor

Conditions: 15% solids UF resin, rayon fabric, cured 10 min./300° F.

No.	Catalyst, 0.1%	HCOONa, %	Oxidizing agent, 0.5%	Reducing agent, 0.5%	Kraus test
VII-1	NH_4Cl	—	—	Sodium hydrosulfite	0
2	NH_4Cl	—	—	Sodium sulfide	0
3	NH_4Cl	—	—	Hydroquinone	0
4	NH_4Cl	—	—	Stannous chloride	0
5	Oxalic acid	—	—	*	0
6	NH_4Cl	0.5		Hydroquinone	++
7	NH_4Cl	0.5		Sodium sulfoxylate	++
8	Oxalic acid	0.5		*	++
9	NH_4Cl	0.5	*p*-Quinone	—	++
10	NH_4Cl	0.5	H_2O_2	—	++
11	NH_4Cl	0.5	$NaBO_3$	—	++
12	NH_4Cl	0.5	NaOCl	—	++
13	NH_4Cl	0.5	$KMnO_4$	—	++
14	NH_4Cl	—	$NaBO_3$	—	+
15	NH_4Cl	—	H_2O_2	—	+
16	NH_4Cl	—	NaOCl	—	0

* The oxalic acid catalyst is also a potential reducing agent.

Another possibility—that a certain oxidizing agent might selectively convert the formate to CO_2 and water and so inactivate it, without oxidizing formaldehyde to formate—was similarly unrewarding (Table VII, Trials 9–13). In fact, in some cases (Trials 14–15) an oxidizing agent produced TMA in the absence of added formate—probably by creating formate from formaldehyde. However, this did not always occur (Trial 16) and in some cases the action of oxidizing agents was erratic (i.e., the effect was marginal or variable).

The Effect of Copper

The original observation of Gruntfest, who obtained a substantial quantity of fish odor when a UF paste was heated to 400° F. in a Parr bomb which accidentally happened to have a copper washer, has been confirmed on several occasions. However, attempts to accentuate TMA production on fabrics by addition of traces of copper sulfate to the pad bath have been relatively unsuccessful. Even on curing at 350° F., only a faint precipitate was produced in the subsequent Kraus test. Manganese sulfate was also inefficient.

To show that formate can be generated by heat, and that copper can accentuate the effect, it was necessary to go to extreme curing conditions. In one experiment, a rayon fabric was treated with a solution of UF resin (deionized) plus 1% diammonium phosphate. Another swatch of the same fabric was treated with a similar bath containing, in addition, 0.01% cupric acetate. Curing for 10 min. at 350° F. failed to give a positive Kraus test in either case, but when the fabrics were subsequently recured 3 min. at 365°, the first fabric gave a slight precipitate, and the second (containing copper) gave a moderate precipitate.

To test the possibility that copper might catalyze oxidation under moist conditions, a fabric was padded through a solution of UF paste resin (deionized) and diammonium phosphate catalyst, plus 0.01% cupric acetate. The fabric was then placed in a bottle and capped loosely. After three days, the fabric—still partially damp—was dried at 240° F. and cured 10 min. at 330° F. Despite the excellent opportunity for regeneration of the formate, the fabric subsequently gave no precipitate in the Kraus test.

TABLE VIII. Effect of Catalyst Type and Concentration on Apparent TMA Formation

Conditions: 15% UF solids, 0.25% sodium formate plus catalyst, cured 10 min. at 300° F.

No.	Catalyst	Kraus test
VIII-1	0.5% $(NH_4)_2HPO_4$	+++ (much)
2	1.0% $(NH_4)_2HPO_4$	+ (some)
3	3.0% $(NH_4)_2HPO_4$	(+) (trace)
4	0.5% $(NH_4)_2HPO_4$ plus 2% tartaric acid	0 (none)
5	0.5% amine hydrochloride	++
6	2.0% amine hydrochloride	(+)
7	1.0% $MgCl_2 \cdot 6H_2O$	+
8	2.5% $MgCl_2 \cdot 6H_2O$	+
9	5.0% $MgCl_2 \cdot 6H_2O$	(+)
10	1% $Zn(NO_3)_2 \cdot 6H_2O$	0
11	0.5% NH_4Cl	+++
12	0.5% NH_4Cl plus 0.1% $Zn(NO_3)_2 \cdot 6H_2O$	++
13	0.5% NH_4Cl plus 0.3% $Zn(NO_3)_2 \cdot 6H_2O$	++
14	0.5% NH_4Cl plus 0.5% $Zn(NO_3)_2 \cdot 6H_2O$	0

Catalyst Effects

As mentioned earlier, the harmful effect of ammonium salt catalyst in accentuating fish odor has long been recognized. However, it has been shown in the aforegoing discussion that avoidance of ammonium salt catalysis will not prevent formation of TMA in cases where sufficient ammonia can be supplied by thermal decomposition of the resin. The only known exception to this is alkaline catalysis (Table V); even in that case it is not clear whether no TMA is formed or whether it forms and immediately volatilizes.

There are two other aspects of catalyst behavior that are not generally recognized. In many instances where a small amount of ammonium catalyst will produce considerable TMA, a large amount of the same catalyst appears to reduce TMA production. Rath was possibly aware of this, as he specified "a little acidity" as one of the conditions leading to odor development. Also, certain metal salt catalysts, notably zinc nitrate and chloride, at times appear to prevent TMA production, even though sources of ammonia, formaldehyde, and formate are present. This phenomenon has not previously been reported. Both of these effects, which are more apparent than real, are illustrated in Table VIII.

Not only does increased concentration of catalyst tend to reduce the amount of TMA in the subsequent Kraus test but, more important, zinc nitrate in suf-

TABLE IX. Regular vs. Modified Kraus Test Results

Conditions: 15% UF solids, 0.25% sodium formate, plus catalyst, cured 10 min. at 300° F.

No.	Catalyst	Kraus test* Regular	Modified
IX-1	3.0% $(NH_4)_2HPO_4$	(+)	++
2	1.0% $Zn(NO_3)_2 \cdot 6H_2O$	0	++
3	0.5% NH_4Cl + 0.5% $Zn(NO_3)_2$	0	++

* The two tests were run consecutively on the same sample. The regular test employed water to hydrolyze the TMA; the modified test employed dilute sodium carbonate.

TABLE X. Ability of Catalysts to Prevent Evolution of TMA During the Kraus Test

No.	Catalyst*	Kraus test† Regular	Modified
X-1	None (TMA only)	0	0
2	0.5% magnesium chloride	+	0
3	1.0% magnesium chloride	+	0
4	5.0% magnesium chloride	+	+
5	0.5% ammonium chloride	+	(+)
6	2.0% ammonium chloride	(+)	+
7	0.5% copper sulfate	+	(+)
8	0.5%copper nitrate	+	+
9	0.5% zinc sulfate	+	+
10	0.5% zinc chloride	0	+
11	0.5% zinc nitrate	0	+

* In every case the hydrated salt was used (e.g., $CuSO_4 \cdot 5H_2O$).

† Run consecutively on the same fabric sample. The data are essentially qualitative, with little attempt to differentiate quantity of precipitate.

ficient quantity seems to prevent TMA production even though all three essential components (NH_4, CH_2O, $HCOO^-$) are present.

These findings were at first very puzzling, until it was realized that considerable TMA was being *formed*, but was not being *evolved*. Instead, it was being held in the fabric by the excess catalyst or the zinc salt. This was rather surprising, in view of the fact that a TMA salt would be expected to hydrolyze during steam distillation, as in the Kraus test. That it did occur, however, was readily demonstrated in the following way: a fabric was treated with a resin formulation containing the three essential components plus the catalyst under study. Following the cure, it was subjected to the Kraus test in the usual way; then to the same flask was added 0.1 g. of sodium carbonate, and a second distillation was conducted. The TMA, released by the alkali, now gave a positive Kraus test. Typical results are shown in Table IX.

An interesting question now presented itself: was the TMA held by the cured resin-catalyst, or by the catalyst alone? To answer this, the problem was reduced to barest essentials: the resin was omitted. Instead, commercial TMA was diluted to 0.1% with water, catalyst was added, and the mixture applied to fabric. The fabric was dried and cured in the usual way, then subjected to regular and modified Kraus test. Many catalysts have been evaluated in this way. Typical results are shown in Table X.

It is readily apparent (Sample X-1) that TMA will not be held on the fabric in the absence of catalyst, as it does not show up in either test. However, all of the catalysts held onto at least some of the TMA. Depending on how tightly they held it, catalysts fell into three general classes: those that permit evolution of all or most of the TMA during the regular Kraus test (e.g., normal amounts of $MgCl_2$ or NH_4Cl); those that release only part of the TMA during the regular Kraus test, leaving part to be evolved in the modified test (e.g., $Cu(NO_3)_2$, $CuSO_4$, $ZnSO_4$, large amounts of $MgCl_2$ or NH_4Cl); and those that hold tightly to the TMA, so that little if any is released during the regular Kraus test (e.g., $Zn(NO_3)_2$, $ZnCl_2$).

The reason for this ability of certain zinc salts to hold onto TMA is not known. Zinc does not appear to form a Werner complex with TMA, as it does with ammonia. Nor does the effect seem to be simply one of pH. For example, the pH of a water extract of the sample containing $ZnCl_2$ (which held onto TMA during the test) was 5.6, while the pH of the sample containing $CuSO_4$ (which did not) was 5.0. This matter has not been further studied.

Regardless of the mechanism, it must be concluded that, quite aside from whatever effect catalysts may have in the *production* of TMA, they can certainly influence the *evolution* of TMA from the fabrics.

The Effect of Resin Type

The data reported thus far concern the application of the usual UF paste resin precondensate to rayon fabric. It has been shown that three components are necessary to produce TMA, and that these interact under the conditions of heat and acidity ordinarily employed to set the resin. Obviously, all of these variables should be kept at as reasonable a level as possible. Yet it is just as obvious that not all of

them are subject to control. Fortunately, it is not necessary to control all of the variables, since complete exclusion of any one essential factor should prevent the formation of TMA.

However, further study has shown that the feasibility of control of the various factors will differ considerably, depending on the type of resin being applied. Indeed, the relative importance of the various factors may also differ. In analyzing this situation, let us begin by reviewing the information already presented concerning the urea-formaldehyde paste resin.

Urea-Formaldehyde

In the case of the simple UF resin (exemplified by the precondensate of low F/U ratio) the possibility of controlling the various factors may be summarized as follows.

Ammonium ion. There is ample evidence that sufficient NH_4 can be evolved by thermal decomposition of the urea of the resin precondensate, so that it would appear impossible to eliminate it entirely. Naturally, other sources of ammonia should be avoided, including use of NH_4 salt catalyst, as these may aggravate the situation.

Formaldehyde. Here again, it seems impossible to avoid its presence, as it can evolve from the UF resin. The data show that addition of urea as a formaldehyde acceptor is not always effective.

Formate ion. This seems to be the only one of the three essential components that can be adequately controlled. The data show that if the UF resin solution is deionized shortly before use, the probability of amine odor formation is negligible. Deionization at time of manufacture if not necessarily effective, inasmuch as formate could gradually be produced by oxidation of the formaldehyde of the resin over a period of weeks or months. This explains the well-known observation that aged UF resin is more prone to produce amine odor on fabric than is fresh resin [1]. Naturally, no formate-containing substances or oxidizing agents should be added to the resin bath.

Heat. The evidence is clear that the higher the cure the more TMA; therefore overcure should be avoided. However, even mild curing will produce TMA if other components are at a sufficient level. The effect of prolonged cure at room temperature has not been studied.

Acidity. Because even mild acid catalysis is sufficient to produce TMA, the only alternative would be to use alkaline catalysis [2]. This gives adequate curing only with simple UF paste types of low F/U ratio. At high cure, some NH_3 may be noticeable. Alkaline cure is ineffective at room temperature [6].

Ethyleneurea-Formaldehyde

The study of ethyleneurea-formaldehyde proved to be somewhat more complicated than was the case with urea-formaldehyde. In setting up an experiment to determine the components necessary for TMA production and the feasibility of controlling them, the following factors had to be considered.

Ethyleneurea is used primarily on cotton, yet a comparison had to be made on rayon to rule out any possible differences (however unlikely) due to type of cellulosic fabric.

In the light of the effect of catalyst in holding onto TMA, it seemed desirable to run both the regular and the modified Kraus tests.

Because urea, added as a formaldehyde acceptor, can serve as a ready source of ammonia, it appeared advisable to substitute dicyandiamide, which is thermally more stable.

To simplify the experiment, copper was eliminated as a variable.

The ethyleneurea-formaldehyde used in this work was a commercial product having a molar F/EU ratio of 2.0 with about 1% free formaldehyde. A 15% solids solution was deionized with Amberlite XE-81 to free it of both cations and anions. Applications to rayon were made at 10% EUF solids, plus the following: (a) where formaldehyde was to be sequestered, 2% dicyandiamide; (b) where ammonia was to be absent, 1% amine hydrochloride catalyst [4]; (c) where ammonia was to be present, 0.25% diammonium phosphate plus 0.75% amine hydrochloride catalyst; and (d) where formate was to be present, 0.25% sodium formate.

Applications to cotton were made using the same padding baths, after dilution with one-third their volume of water. In all cases the fabrics were cured 10 min. at 300° F.

Regular (neutral) and modified (alkaline) Kraus tests were run consecutively on each sample—the modified test liberating whatever residual TMA had not been released in the regular test. Data are given in Table XI. The results of the two tests are separated by commas (e.g., +,+ means positive by both tests).

For comparison, earlier data on corresponding UF treatments (from Table II) are included. As these

[4] 2-methyl-2-aminopropanol-hydrochloride (30%).

data were obtained by a different operator at a much earlier time, the rating scale may not be identical. Nevertheless, a number of clear-cut conclusions may be reached.

First, it will be observed that agreement between the UF and EUF data is excellent in Trials 1 and 2 (no TMA) and in Trials 7 and 8 (much TMA). Also, there is no significant difference between cotton and rayon.

However, in the other cases, two marked reversals appear. In Trials 4 and 6, which are characterized by the fact that *ammonia* has been excluded, the UF treatment nevertheless evolved considerable TMA. The EUF treatments were free of TMA under these conditions. On the other hand, in Trials 3 and 5, which are characterized by the fact that *formate* has been excluded, the EUF treatment showed amine odor whereas the UF did not.

The first of these differences is easily explained. Where ammonia has been excluded, a UF treatment can still produce TMA because the necessary ammonia can be obtained through thermal breakdown of the urea during the cure. The fact that this does not occur in the case of an EUF treatment is evidence that ethyleneurea is thermally more stable than urea.

It must be kept in mind, of course, that stability is a relative quality. A compound that is stable under normal conditions may start to decompose under very drastic conditions, in which case sufficient ammonia may be produced to permit noticeable TMA formation. To explore this possibility, a brief comparison was made of UF, EUF, and two other types of resin under excessive curing conditions. The data, Table XII, show ethyleneurea and melamine types to be quite resistant to thermal breakdown, but verify the hypothesis that very drastic overcure will cause TMA formation even in the case of those resistant materials.

Much additional information has been obtained on the effect of ammonia as a controllable variable in the case of EUF treatments. A typical experiment is outlined in Table XIII.

Many similar experiments have been run. The results in every instance lead to the conclusion that *in the case of ethyleneurea formaldehyde, complete avoidance of ammonia will prevent formation of TMA.* Of course, curing conditions must not be

TABLE XI. Kraus Test Results on Fabrics Treated with UF and EUF in the Presence of Various Components

No.	CH_2O	NH_4	$HCOO^-$	Urea-formaldehyde	Ethyleneurea-formaldehyde	
				On rayon*	On rayon†	On cotton
XI-1	—	—	—	0	0, 0	0, 0
2	X	—	—	0	0, 0	0, 0
3	—	X	—	0	(+), 0	(+), 0
4	—	—	X	+++	0, 0	0, 0
5	X	X	—	0	++, (+)	++, 0
6	X	—	X	+++	0, 0	0, 0
7	—	X	X	+++	++, (+)	++, 0
8	X	X	X	+++	++, ++	++, 0

Scale (for EUF data only): 0 none, (+) trace, + positive, ++ strong positive.
* Regular test only.
† Regular followed by modified test (Na_2CO_3) on same sample.

TABLE XII. Effect of Overcure on Four Resin Types

Conditions: Resin as shown, plus 1% organic amine hydrochloride catalyst and 0.25% sodium formate. Curing as shown. Rayon fabric

No.	Resin type	Amount of solids, %	Kraus test after curing	
			10 min./330° F.	5 min./360° F.
XII-1	Urea formaldehyde	15	+++	+++
2	Methylated urea F.	10	++	++
3	Methylated melamine F.	12	0	+
4	Ethyleneurea F.	10	0	+

overly severe, and other ammonia-forming materials must be absent.

Returning now to the second distinction between UF and EUF—the effect of formate content—further study has confirmed the observation that in the case of the *UF paste resin*, formate is a critical variable: TMA production is proportional to the amount of formate present. Further study of *EUF treatments*, however, shows formate to have an erratic effect: considerable TMA may be produced in the absence of formate, as shown in Trial XI-5, but at other times little or no TMA is obtained, even though ample formaldehyde and ammonia are present.

In the latter case (where little TMA has been obtained despite presence of CH_2O and NH_3), a parallel treatment to which formate has been added will always give a high yield of TMA; thus the lack of reproducibility is not the fault of the Kraus test.

On the other hand, presence of a formaldehyde acceptor (such as dicyandiamide or urea) always reduces the yield of TMA when formate is absent (compare Table XI, Trials 3 and 5) but not when formate is present (Trials 7 and 8).

Considering these facts, it would appear that the production of TMA in systems where formate has been excluded requires a relatively high concentration of formaldehyde. Two possible mechanisms come to mind. During the cure, part of the formaldehyde oxidizes to formate, which then reacts with the ammonia and formaldehyde already present; or where the formaldehyde content is high enough, TMA is produced by direct reaction of formaldehyde and ammonia, as proposed by Rath [7] and Fluck [1].

It has not been possible to distinguish between these alternatives. The effect of certain oxidizing agents (Table VII) lends support to the formate theory, but despite further study (Table XIV) the question is still unresolved. In the latter study, deionized formaldehyde was added to a paste UF bath, which had also been deionized; in some cases an oxidizing agent (sodium perborate) was also added. Diammonium phosphate was used as catalyst and source of ammonia. Curing was 10 min. at 330° (quite severe) to accentuate the effect. From the data (Table XIV) it may be seen that an increase in TMA results from addition of formaldehyde, especially if an oxidizing agent is present, but the yield of TMA is not nearly so pronounced as when a little sodium formate is added at the outset.

Similar experiments have been run with the ethyleneurea type. A rather complicated example is shown in Table XV. Here were compared a normal EUF product, one with less formaldehyde, and one with more. Comparisons were also made of the effect of dicyandiamide in reducing the CH_2O content, of perborate in increasing the formate content, and of absence of ammonia. The results were about

TABLE XIII. Ammonium Catalyst as a TMA Component

Conditions: 6% EUF, 0.25% HCOONa, plus catalyst as shown. Cured 10 min./300° F. Cotton fabric

No.	Catalyst	Kraus test
XIII-1	0.5% ammonium chloride	++, 0
2	0.5% diammonium phosphate	++, 0
3	1.0% amine hydrochloride (30%)	0, 0
4	1.0% magnesium chloride	0, 0
5	2.0% $MgCl_2$ plus 0.5% NH_4Cl	++, 0
6	0.5% $Zn(NO_3)_2$ plus 0.5% NH_4Cl	0, ++

TABLE XIV. Effect of Additional Formaldehyde and Oxidizing Agent

Conditions: Rayon fabric, 10% paste UF solids, 1% $(NH_4)_2HPO_4$. Cured 10 min. at 330° F.

No.	Additives: % CH_2O (37%)	Additives: % $NaBO_3$	Additives: % HCOONa	Kraus test*
XIV-1	0	—	—	0, (+)
2	1	—	—	0, +
3	3	—	—	0, +
4	0	0.25	—	0, (+)
5	1	0.25	—	(+), +
6	3	0.25	—	+, ++
7	0	—	0.25	+++, ++

* Regular, modified run consecutively as described earlier; legend as given in Table XI.

TABLE XV. Miscellaneous Experiments in Controlling Components That Produce TMA

Conditions: Cotton fabric, 5% EUF solids (deionized), 0.5% amine HCl plus 0.5% $(NH_4)_2HPO_4$. Cured 10 min. at 330° F.

No.	Variable	Kraus test
XV-1	Conditions as listed above (standard)	+, +
2	Ammonium salt omitted	0, 0
3	0.25% $NaBO_3$ added (to increase formate content)	++, +
4	2% Dicyandiamide added (to sequester formaldehyde)	(+), 0
5	2% CH_2O (37%) added (to raise formaldehyde content)	++, +
6	2% CH_2O (37%) + 0.25% $NaBO_3$ (increase CH_2O and formate)	+++, ++
7	EUF having F/EU ratio of 1.75 (less formaldehyde)	+, +

as expected; the question of whether or not formate is necessary was not resolved.

If oxidation of formaldehyde to formate is involved, it is difficult to control. Traces of copper or manganese will not accelerate it under mild curing conditions. Moreover, as indicated earlier (Table VII), sodium hypochlorite cannot be substituted for perborate, and in other instances the action is erratic. What is required is an oxidation system that yields formate without interfering with the subsequent TMA reaction, which appears to be a reduction. The matter has not been further studied.

From a practical standpoint, it is obvious that in the case of the EUF product—which contains considerable formaldehyde—deionization of either the resin or the padding bath is a relatively ineffective way of avoiding amine odor.

There are two remaining variables—heat and acidity. As to the first of these, evidence has already been presented (Table XII) that drastic overcure can be harmful and so should be avoided. However, the same data also reveal that, in the absence of ammonia, little or no TMA will be formed even under curing conditions that would be considered quite severe (10 min. at 330° F.). Ethyleneurea formaldehyde is much safer than urea formaldehyde in this regard, and it is probable that the reduced incidence of amine odor over the past several years is due in large part to the increased use of EUF plus nonammoniacal catalysts.

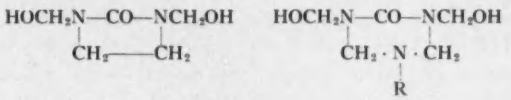
As to acidity, the same rule applies as with urea formaldehyde: the type and concentration of catalyst have more effect on *evolution* of TMA than they have on its *formation*. Thus, if an EUF resin is applied in the presence of small amounts of ammonium salt and formate (so that CH_2O, NH_3, and $HCOO^-$ are all present) the addition of 0.25–0.5% zinc nitrate will prevent TMA from showing up in the regular Kraus test. Only in the modified test, where soda ash is added to the distillation flask, will TMA evolve. Thus, the use of zinc nitrate catalyst in the absence of ammonium salt should give double protection: no TMA will form if NH_4 is completely excluded, but if traces of NH_4 should creep in through overcure or through bath contamination, the zinc salt will tend to prevent the TMA from evolving until the fabric is given its first laundering. However, the question of whether a given resin-catalyst combination will insure freedom from amine odor in the absence of afterwashing can be decided only on the basis of extended field testing under all conditions of consumer use.

In this connection, it should be emphasized that there is no practice as safe as that of thorough afterwashing, using sufficient alkali to volatilize any TMA and then rinsing to leave the fabric neutral or just slightly alkaline. But in many cases, for expediency, fabrics are merely padded through an alkaline solution and dried without rinsing. This is the worst possible practice, as it frees the TMA without washing it out, thus permitting gradual evolution over a period of days. No catalyst can protect against this. It is undoubtedly safer—from the standpoint of amine odor—to leave the fabric on the acid side than to merely neutralize it without rinsing. (The effect of such practice on formaldehyde odor, chlorine retention, and other properties is outside the scope of the present discussion.)

As stated earlier, no afterwash was given the fabrics in the experiments described above, since we wanted to measure the entire TMA content resulting from the various treatments.

Triazone-Formaldehyde

A newer type of creaseproofing agent is the so-called triazone. Whereas ethyleneurea has two nitrogens in a 5-membered ring, the triazone—which is also a cyclic urea—has three nitrogens in a 6-membered ring.



There are a number of these on the market, varying in composition and purity, and it is too early to make all-inclusive statements concerning them. However, there is considerable evidence that most if not all members of this class tend to produce a certain amount of amine odor, regardless of attempts to control the formate, ammonia, or free formaldehyde contents.

The amine odor is not necessarily due to TMA; in fact, the compound responsible for the odor will probably differ depending on the composition of the triazone. The positive Kraus test suggests that at least some tertiary amine is present. This might be formed directly, through thermal breakdown of the triazone during application to the fabric; by reaction of primary amine, from such breakdown, with formate and/or formaldehyde; or by reaction

of primary amine, present as an impurity in the original product with formate and/or formaldehyde. The amine would in such cases have the identity $(CH_3)_2NR$, where R will vary according to the type of triazone.

In addition, where ammonia is present, some TMA may be produced by the reaction of ammonia with formate and/or formaldehyde described earlier.

It should be kept in mind that complications can conceivably arise in using the Kraus test to judge amine odor in triazone finishes. For example, the test may be less sensitive to certain amines than to others, so that the concentration of amine will appear to be lower than it actually is. Conversely, some amines may have a less objectionable odor than others, yet the Kraus test cannot show this. For these reasons, Kraus test results on fabrics finished with triazones should be assessed cautiously, and confirmed by smelling a few drops of the distillate during the first part of the test. A positive test should be accompanied by an amine odor.

As mentioned earlier, attempts to control formate, ammonia, or formaldehyde contents are useless. Moreover, the amount of amine produced is usually too great to be held by zinc nitrate or similar catalyst. It is obvious, therefore, that fabrics finished with triazones should be given a thorough alkaline after-wash, preferably at 160° F., if amine odor is to be avoided.

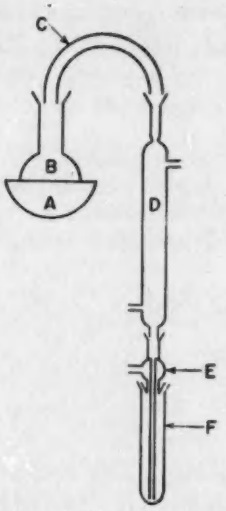


Fig. 1. Kraus test apparatus. Ground-glass connections should be used. The outlet tube E should extend almost to the bottom of tube F. A—heating mantle, B—300-ml. round bottom flask, C—wide curved glass tube, D—condenser, E—outlet pipe, and F—test tube.

Other Resin Types

Insufficient study has been made of melamine- and methylated urea-formaldehyde resins to permit the drawing of more than a few general conclusions. Because melamine is thermally stable (Table XII) it seems likely that avoidance of ammonia will insure freedom from amine odor. The effects of methylation and of formaldehyde content are more difficult to assess. A methylated UF having high Me/U and F/U ratios showed slightly less tendency to produce amine odor than did a paste resin of low F/U content, when ammonia was absent and formate ion was present (Table XII). But it has not been determined whether a high formaldehyde content will tend to produce some amine odor in *absence* of formate, as was the case with the ethylene urea type. Nor has it been established whether methylation would tend to prevent this.

Appendix

The Kraus Test for Trimethylamine

The test used throughout this work is essentially that described by Kraus, except that a larger fabric sample was used together with proportionately larger amounts of chemicals. The principles of the test and the apparatus and procedure by which it was carried out are given below.

Principles of the Test

The fabric to be tested is boiled in water to hydrolyze amine salts. The steam distillate, containing the liberated amines, is carried over into a solution of iodine in potassium iodide, where periodides of the amines are formed. The periodide of TMA is quite insoluble and shows up as a dark brown precipitate. The periodides of di- and mono-methylamine are more soluble, and will usually not be detected unless present in large amounts.

Ammonia will give a greenish black precipitate if carried over; this is prevented by adding mercuric oxide to the distillation flask. Formaldehyde, which will interfere with the formation of the precipitate, is held back by melamine added to the flask.

Chemicals Required

Solution A (solution of iodine in potassium iodide)

Dissolve 6 g. KI in 40 ml. distilled water; then add 5 g. iodine. When dissolved, dilute to 440 ml.

with distilled water. This should preferably not be kept longer than one week.

Solution B (melamine-mercuric oxide suspension)

Stir 60 g. HgO and 80 g. melamine into 1 l. of distilled water. This mixture must be stirred thoroughly just prior to use, and must not be kept longer than 48 hr.

Apparatus

The apparatus, assembled, is shown in Figure 1.

Procedure

Cut a 10-g. sample of the test fabric into small pieces (1 × 1 in. or smaller) and place in flask B. Add 75 ml. of solution B and shake flask to insure thorough impregnation of the fabric. To tube F add 6 ml. of solution A. Heat the flask to the boil and collect 3 ml. of distillate in tube F. If TMA is present, a dark brown precipitate will form.

If the precipitate has a greenish appearance, it usually indicates that there has been some carry-over of ammonia. In this case, addition of a few milliliters of solution A to the tube will cause it to dissolve.

Comments

The test as visualized by Kraus is essentially a qualitative yes-or-no test. However, throughout most of our work we attempted to make rough semi-quantitative estimates of the amount of precipitate. No absolute standards were set up, and the data are more reliable for comparisons within an experiment than between experiments. In one case where known concentrations of TMA were added directly to the collection tube and compared with visual ratings, the following relationship was observed:

Actual TMA, mg.	Visual rating
0.4	(+)
0.6	+
0.9	++

These should be taken as order-of-magnitude values only, as they do not necessarily hold for different operators or for the same operator at different times. Moreover, other experiments showed that in some instances slightly higher amounts of TMA may be required on the fabric to obtain the same ratings, indicating that not all of the amine is carried over in the 3-ml. distillate.

On occasion, a faint precipitate was observed, which then disappeared by the time 3 ml. of distillate had been collected. Throughout the present study we arbitrarily considered this a negative result, although it is possible that in most instances a very small amount (0.1–0.3 mg.) of TMA was present.

In regard to the modified test in which 0.1 g. sodium carbonate was added to the distillation flask, we have not had enough experience with this to recommend it as a replacement for the regular test. Its chief use has been as a supplemental procedure to detect residual TMA not hydrolyzed in the regular procedure. We might expect that the alkaline conditions would drive over ammonia and thus give a false precipitate. This has happened on occasion, though with gratifying rarity. The possibility of other such complications due to the alkalinity must be kept in mind.

In regard to the greenish precipitate, there have been a few cases where such a precipitate was obtained which did not appear to be due to ammonia, as it did not redissolve. Nor was it due to dimethylamine, which yields a brown precipitate when present in sufficient quantity. We have no ready explanation for the phenomenon. Such results were reported as positive tests for TMA.

Theoretical Considerations

Rath [7] stated that amine odor in resin-treated textiles is due to the presence of methylamines, especially trimethylamine, which are formed in the following fashion.

"During reaction of ammonia or ammonium salts with formaldehyde, under certain conditions, the hydrogen atoms of the ammonia are successively replaced by methyl residues according to the following equations:

1. $2NH_3 + 3CH_2O = 2CH_3NH_2 + CO_2 + H_2O$ (monomethylamine)
2. $2NH_3 + 6CH_2O = 2(CH_3)_2NH + 2CO_2 + 2H_2O$ (dimethylamine)
3. $2NH_3 + 9CH_2O = 2(CH_3)_3N + 3CO_2 + 3H_2O$ (trimethylamine)

"The corresponding salts of these bases are formed by customary applications of ammonium salts, e.g.,

$$2NH_4Cl + 9CH_2O = 2(CH_3)_3N \cdot HCl + 3CO_2 + 3H_2O$$

"The possibility of a reaction according to Equation 3 increases with increasing excess of formalde-

hyde, i.e., with respect to the formation of large amounts of trimethylamine. Mono- and dimethylamine are present in smaller amounts since they continue to be methylated by formaldehyde to form trimethylamine."

Fluck, Keppler, Cooke, and Zimmerman [1] postulated the formation of methylamines from ammonia plus formaldehyde or methyl alcohol, with hexamethylene tetramine as one of the several possible intermediates. They proposed the following reactions:

A. (1) $2NH_4Cl + 3CH_2O/aq. \rightarrow 2CH_3NH_2 \cdot HCl + CO_2 + H_2O$

(2) $2NH_4Cl + 6CH_2O/aq. \rightarrow 2(CH_3)_2NH \cdot HCl + 2CO_2 + 2H_2O$

(3) $2NH_4Cl + 9CH_2O/aq. \rightarrow 2(CH_3)_3N \cdot HCl + 3CO_2 + 3H_2O$

(4) $3CH_2O + 2CH_3NH_2/aq. \rightarrow 2(CH_3)_2NH + CO_2 + H_2O$

(5) $3CH_2O + 2(CH_3)_2NH/aq. \rightarrow 2(CH_3)_3N + CO_2 + H_2O$

B. (1) $NH_4Cl + 2CH_2O \rightarrow CH_3NH_2 \cdot HCl + HCOOH$

(2) $NH_3 + HCOOH \rightarrow HCOONH_4$

(3) $CH_2O + HCOONH_4 \rightarrow CH_3NH_2 + CO_2 + H_2O$

C. (1) $CH_3OH + NH_3/cat. \rightarrow CH_3NH_2 + H_2O$

(2) $CH_3OH + CH_3NH_2/cat. \rightarrow (CH_3)_2NH + H_2O$

(3) $CH_3OH + (CH_3)_2NH/cat. \rightarrow (CH_3)_3N + H_2O$

D. (1) $6CH_2O + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$

(2) $(CH_2)_6N_4 + HCl + 4H_2O \rightarrow 4CH_3NH_2 \cdot HCl + 2CO_2$

It will be observed that in only two cases (Series B) is formate mentioned; it is a product of reaction B-1, rather than a component, and it then reacts to form monomethylamine in B-2 and B-3.

Yet Fluck et al. were well aware that presence of formate increases amine odor, and emphasized that it should be excluded from treating baths.

In the light of the present evidence that formate is an essential ingredient to the production of trimethylamine in the case of the usual paste UF resin, and an important contributing factor in the case of the EUF type, it is quite likely that the Leuckart reaction is involved. This is the reductive alkylation of ammonia or amines by aldehydes or ketones, utilizing formic acid as the reducing agent.

Two mechanisms for this reaction have been suggested [5]. In the first of these, formic acid is merely a reducing agent:

$$NH_3 \xrightarrow{CH_2O} HOCH_2NH_2 \xrightarrow{HCOOH} CH_3NH_2$$

$$CH_3NH_2 \xrightarrow{CH_2O} HOCH_2NHCH_3 \xrightarrow{HCOOH} (CH_3)_2NH$$

$$(CH_3)_2NH \xrightarrow{CH_2O} HOCH_2N(CH_3)_2 \xrightarrow{HCOOH} (CH_3)_3N$$

In the second, formic acid plays a more essential role, forming a series of intermediates (substituted amides) as well as acting as a reducing agent:

$$NH_3 \xrightarrow{HCOOH} HCOONH_4 \xrightarrow{-H_2O} HCONH_2 \text{ (formamide)}$$

$$HCONH_2 \xrightarrow{CH_2O} HCONHCH_2OH \xrightarrow{HCOOH} HCONHCH_3 \text{ (methyl formamide)}$$

$$HCONHCH_3 \xrightarrow{CH_2O} HCONCH_2OH \xrightarrow{HCOOH}$$

$$\text{(dimethylformamide) } HCON(CH_3)_2$$

$$HCON(CH_3)_2 \xrightarrow{H_2O} NH(CH_3)_2 \xrightarrow[HCOOH]{CH_2O} HOCH_2N(CH_3)_2 \rightarrow N(CH_3)_3$$

The difficulty with the latter mechanism, plausible though it may seem in accounting for the specificity of formic acid over other reducing agents, is that the last step is impossible under the conditions of resin application. Thus, equimolar quantities of dimethylformamide, formaldehyde, and formic acid in water solution, applied to cotton fabric and cured (10 min./300° F.), will not produce sufficient TMA to show up in the Kraus test.

It would be much more simple to accept the view that most of the TMA is formed directly through the reaction of ammonia and formaldehyde, or even of ammonia and methanol. Such reactions are carried out industrially, but good yields are not obtained unless temperatures and pressures are far above those employed in textile processing. On the other hand, the reaction between ammonia, formaldehyde, and formic acid appears to take place readily at moderate temperatures and atmospheric pressure, with a good yield of trimethylamine and negligible amounts of mono- and dimethylamine [8]. On the basis of the evidence presented herein, this may well be the chief source of trimethylamine in resin-treated fabric.

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Epoxy Resin Blended Finishes for White Cottons[1]

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Abstract

New finishes based on blends of epoxy resins with selected aldehydes, acetals, formaldehyde-amino resins, hemiacetals, and polymeric materials such as silicones, polyethylene, polyacrylates, and epoxy based plasticizers have been explored to produce new and improved effects on white cotton fabrics. With some of the formulated blends, durable wash-and-wear finishes, crease resistance, and dimensional stability are obtained which will stand repeated laundering and chlorine bleaching operations. An outstanding finish for white cottons has been developed based on combinations of epoxy resins with dimethylol ethylene urea.

The practical conditions of cloth preparation, drying and curing cycles, choice of catalysts, washing procedures, and afterfinishing operations are described for obtaining optimum results. Also discussed are the limitations of these and other presently available finishes for cotton, with special emphasis on some theoretical possibilities for new cotton fiber modification.

Introduction

At the 1956 Chemical Finishing Conference of the National Cotton Council, a paper was presented by Schroeder and Condo describing the use of water soluble epoxy resins for the creaseproofing of cotton [9]. Since that time, there has been a considerable amount of commercial success in utilizing one such resin for the finishing of white cotton fabrics. This product, which is only one of a whole family of diglycidyl ethers of polyols, has been particularly useful for producing stabilized, creaseproof, and wash-and-wear finishes on white cotton fabrics for men's shirts, bed sheeting, knit goods, dresses, and work clothes [10].

[1] Presented at the Chemical Finishing Conference of the National Cotton Council, Washington, D. C., October 2, 1958.

The most outstanding properties of the epoxy resins for use in cotton finishing include the following:

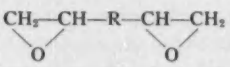
a. complete durability of the finish to laundering
b. complete resistance to damage by chlorine bleaches
c. complete absence of amine or formaldehyde odors

The first two properties result directly from the reaction of epoxy groups with cellulose to give stable nonhydrolyzable bonds, and from the nonnitrogenous nature of the compounds which prevents chloramine formation in bleaching. The third property results from the absence of any residue in the epoxy struc-

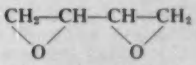
ture which could give odoriferous byproducts in curing or in practical use of the treated fabric.

In contrast to these very desirable properties, the one single major drawback which has prevented wider spread use of epoxy resins in textile finishing is that of cost. Compared to existing cotton finishing resins such as the dimethylol ethylene urea, the methylated polymethylol ureas, and the melamine resins, those epoxy resins useful for cotton finishing have considerably higher raw material and manufacturing costs. Beside the higher cost of the resins themselves, the cost of finishing cotton fabrics for wash-and-wear effects is also brought about by the high concentration of epoxy solids needed to give high level of crease resistance and wash-and-wear performance. The need for using higher solids concentrations of epoxy resins than are necessary with such products as the dimethylol ethylene ureas results directly from the higher molecular weight of the epoxy resins. Compare, for example, the average molecular weight of a suitable epoxy resin, of range 300–400, to the molecular weight of dimethylol ethylene urea, which is 146. If the latter product, at 5% applied solids, gives a certain high level of finishing performance on a cotton fabric, then about 12–15% epoxy resin solids are required to equal this performance, since the molecular weight of the epoxy resin is about 2–2½ times that of the dimethylol ethylene urea. It has been previously shown that in those properties of cellulosic fabrics which are altered by cross-linking agents, there is a direct relation between the number of moles of cross-linking agent applied and the degree of modification produced [4], regardless of the chemical nature of the cross-linking agent.

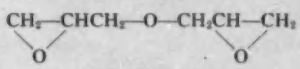
In view of the high molecular weight of those diepoxides found useful for cotton finishing and the resulting high concentrations needed for practical applications, the problem would seem to be a simple one of synthesizing or finding more efficient diepoxy compounds of lower molecular weight. If we consider the basic structure of a diepoxide cellulose cross-linking agent to be



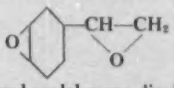
then the most efficient compound to use would be one where the R group, to which the epoxy groups are attached, is very small. Some examples are



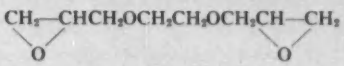
Butadiene dioxide



Diglycidyl ether

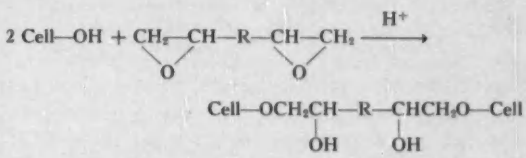


Vinyl cyclohexene dioxide



Glycol diglycidyl ether

where the molecular weights of such pure difunctional cross-linking agents are 86, 130, 140, and 174 respectively. Many of such lower molecular weight diepoxides have been investigated. They all give indications of acting as cellulose cross-linking agents according to the general reaction



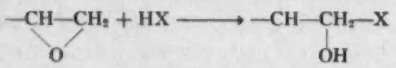
This is evidenced by the reduction in swelling of the cotton cellulose, the increase in elastic performance, the increase in resistance to wrinkling or creasing, the stabilization against shrinking in washing, the insolubility in cellulose solvents, and the immunization against direct dyeing with cellulose substantive dyes.

While these and other lower molecular weight diepoxides do yield potentially more efficient products for creaseproofing and for wash-and-wear finishes for cotton, they also introduce new problems which have prevented their practical applications. The two most serious of these problems are those of toxicity and volatility. Many of the lower diepoxides have individual characteristic vapor or skin toxicity, which would prevent their use in textile plants. Others are sufficiently volatile that they leave the cloth during the drying operation, so that much of the chemical is wasted by evaporation. A third problem is again one of raw material and manufacturing costs, since some of the simple diepoxides are more difficult to manufacture.

Blended Finishes

Since the available epoxy resins which are already in use for finishing white cottons have demonstrated their technical utility, and since their major problem was primarily one of cost, a broad study was initiated to find means of utilizing them in conjunction with other textile finishing chemicals under conditions where the finishing cost might be greatly reduced without altering any of the desirable properties of the pure epoxy resins.

In considering other chemicals which might be blended with epoxy resins, it was thought that any compound containing active hydrogen groups might be potentially useful for blending. This was based on the known reactivity of the oxirane group:



Here the HX compound with active hydrogen could include those containing the following functional groups:

Carboxyl	RCOOH
Alcohol or methylol	R—CH_2OH
Amino or amide	R—NH_2 (R_2 = NH)
Aldehydes	R—CHO
Ketones	$RCH_2\overset{\overset{O}{\|}}{C}CH_2R$
Active methylene	R—CH_2—R
Alkoxy	RCH_2OR
Sulfhydryl	R—SH

Beside these generic classes of active hydrogen containing potential modifying agents, there is a host of other reactive products which independently react with cellulose or form resinous products on curing. Some of these are already in use in cotton finishing. Here it was thought that some of these actual or potential textile finishing agents might give synergistic or unexpected desirable effects if combined with the water soluble epoxy resins. This list includes:

Dialdehydes, such as glyoxal and glutaraldehyde
Formaldehyde, or its acetals and hemiacetals
Methylol ureas
Methylol melamines
Alkoxymethyl ureas and melamines
Dimethylol ethylene ureas
Bis alkoxymethyl urons
Dimethylol triazone condensates
Acetylene diurea-formaldehyde condensates
Acetone-formaldehyde resins
Acrolein-formaldehyde resins
Bis phenol A epoxy resins
Epoxy alkanes
Ketene dimers
Tetralkoxy propane, butane, etc.
2,5-Diethoxy tetrahydrofurane
Spiro acetals of pentaerythritol
Formals of polyols
Dimethylol *p*-cresol
Tetramethylol bis phenol A
Isocyanates

A few of these compounds can undergo all three varieties of reactions if cured on cotton in the presence of the epoxy resins; i.e., reaction with cellulose, reaction with epoxy groups, resin formation, or combinations of all three.

In considering the investigation of some of these compounds or products as additives to epoxy resins for cotton finishing, it was already known in a few cases that such combinations might not be fruitful. The methylol urea resins, for example, are so highly chlorine retentive that their use would be precluded. Some of the dialdehydes might be useful in low concentrations, but not in high amounts, because of their color producing properties. Selected compounds whose reaction with cotton cellulose we have already separately characterized were considered presently impractical because of costs and availability. This includes 2,5-diethoxy tetrahydrofurane, which is an excellent cotton cross-linking agent under the select application conditions we have devised (to be published later) and some of the spiro acetals of pentaerythritol [5].

A large number of products have by now been examined. We will report here only a few of those which have reached commercial utilization as blended epoxy finishes for white cotton fabrics. In this phase of the report we will be concerned primarily with creaseproofing and wash-and-wear effects. Here the attempt was to devise blends which could yield all the desirable properties of the pure epoxy resins but be considerably lower in cost. Table I shows the creaseproofing and other effects produced by two different water soluble epoxy resins applied at different pad bath concentrations. What we have tried to produce is the performance of the 15% epoxy concentration in Table I but by utilizing lower amounts of epoxy resin combined with other additives and without altering the nonchlorine damaging features of the finish.

Materials and Methods

The epoxy containing materials used in this investigation are commercially available products. The major proportion of the formulations used contained Eponite 100, a relatively highly water soluble polyepoxide manufactured by Shell Chemical [10]. Formulations containing Eponite 100 or other epoxy materials, either alone or in conjunction with coreactants, were prepared by emulsifying the epoxy component with 35% saponified, low molecular weight polyvinyl alcohol. Although some commercially available polyepoxides contain as high as 85–90% water soluble fractions at textile use concentrations, it is preferable to utilize an emulsion form of such resins to avoid oil spotting of fabrics by the small water insoluble portion present.

The coreactants used were also commercially available materials. These are identified hereafter by their commonly known names. Zinc fluoborate is the preferred catalyst for epoxy materials when they are used alone and also when used with most coreactants on cotton fabrics. Except where indicated in the data, softeners, lubricants, and hand modifiers were not used in this work. A large selection of such additives is available for use with epoxy resins. They were avoided here for the purpose of simplification. The textile finishing additives commonly used with other resins are, in most cases, compatible and effective with epoxy resins. Two outstanding exceptions are the lack of adequate compatibility of many thermoplastic resin emulsions and the lack of effectiveness of water repellents. Water repellency, when desired, can be imparted by further treatment of the fabric after the epoxy treatment is completed.

The epoxy and epoxy blend finishes were processed in the same manner as the better known thermosetting resins. After impregnation at 70% wet pick-up, the fabrics were frame dried and cured. Optimum curing times and temperatures were found to be identical to those used with other resins. Afterwashing was usually employed to remove residual catalyst and unreacted resins. This consisted of a 0.25% sodium perborate + 0.1% nonionic surfactant process wash followed by rinsing and frame drying. Satisfactory results have been obtained through the use of selected brightening agents and the elimination of the afterwashing step in processing. No problems relative to odor development have arisen even with the use of aminoplasts or other normally odor-creating materials such as formaldehyde, as long as these were used in minor proportion of the total finishing mix.

TABLE I. Typical Performance of Two Water Soluble Epoxy Resins on 80 × 80 Cotton

Resin concentration in bath	MCRA (W+F)	W+F tensile strength, lb.	
		Original	After chlorine test*
10% DMEU Control	264	61	0
7.5% Eponite 100	228	—	—
10.0% Eponite 100	232	—	—
12.5% Eponite 100	251	—	—
15.0% Eponite 100	256	55	59
7.5% D-1	205	—	—
10.0% D-1	236	—	—
12.5% D-1	255	—	—
15.0% D-1	260	54	58

* Two alkaline 200° F. launderings, then AATCC chlorine test and scorch.

The conventional grab tensile strength, Monsanto Crease Recovery Test (MCRA), and Elmendorf Tear Test were used to evaluate these epoxy blended finishes on cotton. Since industry-wide acceptance has not been given to any one laundering procedure to determine the durability and chlorine damage resistance of thermosetting finishes, the test fabrics were subjected to several different laundering and bleaching procedures in an effort to include the various types of laundering possible. This also insured that the chlorine resistance tests were sufficiently severe that unquestionable protection against damage or discoloration by chlorine bleaching was obtained, if so indicated by the test results. The laundering procedures used were as given below.

FSW/Alk

Two consecutive washing cycles of 40 min. each in a reciprocating dash wheel at 200–210° F. with mild soap and soda ash, followed by rinsing, framing, and air drying for 5 min. at 250° F., were used.

Home

Twenty consecutive, complete cycles in an automatic home washer (normal fabric, medium load, hot wash temperature (140° F.), warm rinse temperature, 8-min. wash cycle) with mild soap and washing soda were made. The fabrics were frame dried for 5 min. at 250° F. after the last complete cycle only.

TABLE II. Epoxy Blends with Aldehydes

Resin blends, 10% epoxy and 5% coreactant	MCRA (W+F)	Tensile strength, warp, lb.
No coreactant	225	31
Formaldehyde (37%)	239	28
Glyoxal (30%)	220	32
Glutaraldehyde (25%)	242	28
15% Epoxy control	233	30

TABLE III. Epoxy Glutaraldehyde Blends

Resin blends, 10% epoxy and x% dialdehyde solids	MCRA (W+F)
No coreactant	225
1.0% Glutaraldehyde	248
2.5% Glutaraldehyde	258
5.0% Glutaraldehyde	284
Untreated control	160
15.0% Epoxy control	233

TABLE IV. Epoxy Blends with Amino Resins

Resin blends, 10% epoxy and 5% coreactant	MCRA (W+F)	Tensile strength, warp, lb.
No coreactant	225	31
LV Methylated UF (50%)	246	31
MV Methylated UF (80%)	246	30
HV Methylated UF (80%)	243	32
Methylated MF (75%)	233	33
Modified MF (80%)	270	31
Methoxy methyl uron (50%)	245	29
Dimethylol EU (50%)	245	29
Triazone–HCHO (40%)	230	31
15% Epoxy control	233	30

Home (Cl_2)

Twenty complete cycles in an automatic home washer (as above) with mild soap and chlorine type bleach as recommended by the manufacturer were used. One wash was carried out each day for 5 days each week until 20 washings were completed. After each washing the fabrics were air dried at room temperature for 4 hr. and then ironed for 30 sec. (cotton setting) with a flat bed home ironer.

The resistance to damage by chlorine bleaching, both before and after washing, was determined by the AATCC Tentative Test No. 69-1952. Fabrics laundered in the presence of chlorine bleach were evaluated for tensile strength loss directly without being further subjected to the AATCC test.

The fabric used throughout these investigations was an 80 × 80 kier-boiled, desized, and bleached cotton print cloth. All tests were made following the usual constant humidity and temperature condition cycles. The test result figures represent the average of 3–6 replicate determinations.

Results and Discussion

Nonnitrogenous Coreactants

Of the many types of nonnitrogenous coreactants that might be useful with epoxy resins, the aldehydes were of special interest because of their low molecular weight, low cost, and high efficiency. In attempting to utilize formaldehyde in various forms, it soon became apparent that this would have limited practical use because of the objectionable odor introduced in processing. By using methyl or propyl hemiformals to replace aqueous formaldehyde, the odor could be minimized and possibly be tolerated at low concentrations. Of the aldehydes examined, however, only glutaraldehyde appeared to have practical applications. This is shown by the data in Table II, where the epoxy resin solids have been reduced from 15% to 10% and then 5% of the commercial dilute aldehyde products have been substituted in their place. Under these conditions the effects of 15% epoxy could be matched by the combination finishes.

In Table III are shown the results obtained with different concentrations of glutaraldehyde. Here it is seen that very large improvements in the crease resistance could be obtained by the epoxy-glutaraldehyde blends. At the low concentrations of less than 3%, no particular color problem was found. At higher solids, however, the glutaraldehyde yellowed white fabrics excessively, and the discoloration could not be removed completely by a process wash with sodium perborate. From these results, a satisfactory nonchlorine-retentive finish for white fabrics has evolved using 10% epoxy resin and 2% glutaraldehyde. When combined with other additives, such as silicones, polyethylene, or epoxidized soy bean oil, this blended finish yields crease recovery of 250–270° and excellent wash-and-wear properties.

Nitrogenous Coreactants

A large number of thermosetting resins or fiber cross-linking agents based on nitrogen-formaldehyde products have been examined in combination with several epoxy resins. While many of these are objectionable from the point of view of maintaining resistance to chlorine damage, their enhancement of

crease resistance properties made them interesting for further exploration. Table IV shows the results of blends of 10% epoxy resin with 5% of various commercially available resins. These combinations, in general, give as good or better creaseproofing performance than 15% of the pure epoxy resin. Since several of these coreactants such as the dimethylol ethylene urea, the dimethylol triazone, and the methylated melamine-formaldehyde resin already have fairly good chlorine resistance under certain conditions, the possibility existed of developing an epoxy blend which might give superior performance to either product used alone.

In Table V are shown the results of further tests made with 10% pad bath solids of various combinations of an epoxy resin and dimethylol ethylene urea in one case and a commercial triazone-formaldehyde product in another. The latter products, loosely called triazones, have been commercially available since 1952 and have found uses in finishing white cotton fabrics. The chemistry of triazones and some of their effects on fabrics have been discussed by Paquin [8], Burke [1], and Gagliardi [3]. Their slightly basic character makes them useful in neutralizing some of the acid formed on cotton during ironing of a chlorinated fabric and thereby maintaining higher fabric strength. At the constant 10% solids, it is seen that a remarkable improvement in crease resistance is obtained even at low ratios of DMEU and the epoxy resin. This reaches a maximum at the 5/5 ratio of the two products. In contrast to these results, the epoxy/triazone combinations yielded no improvement in crease resistance. In no cases were the results better than those of the pure epoxy finish.

Since, in these blended finishes, we have used a constant amount of zinc fluoborate catalyst, it was possible that the inefficiency of the triazone resin might be due to its buffering effects during curing. Consequently the series of epoxy/triazone blends was rerun using both the recommended concentration of zinc fluoborate needed for the epoxy plus the recommended amount of special catalyst needed for the triazone. The results of these tests are shown in Table VI. Here it is seen that considerably better crease resistance was obtained with the added catalyst at the high triazone/epoxy ratios. At the lower ratios, however, very few differences were found. These results would indicate the possibility of using some epoxy/triazone blends. Because of the objectionable odor of the triazone treated fabrics, however, and because of the poor effects at low ratios, no further explorations were made of this combination finish.

TABLE V. Epoxy/DMEU and Epoxy/Triazone Blends

Resin blends, epoxy/other solids	MCRA (W+F)	
	DMEU	Triazone
10/0	226	226
9/1	252	208
8/2	267	211
7/3	268	221
6/4	275	217
5/5	276	224
0/5	261	—
0/9	—	263

TABLE VI. Epoxy : Triazone Blends—Different Catalysts

Resin blends, epoxy/other solids	MCRA (W+F)	
	Triazone I	Triazone II
10/0	226	232
9/1	208	212
8/2	211	223
7/3	221	255
6/4	217	253
5/5	224	274
0/9	263	274

In view of the possibility of utilizing some blends of low concentrations of epoxy resin with other known creaseproofing agents for cotton, a detailed study was made of three commercially available resins representing three different classes of materials. These included dimethylol ethylene urea, a methylated trimethylol melamine, and a methylated polymethylol urea. In all cases, the total solids contents were maintained at 10%, but the ratio of epoxy was varied.

Figure 1 shows the improvement in crease resistance produced by increasing the ratio of coreactant to epoxy resin. The combinations of epoxy resin with DMEU were outstanding in this property and superior to either of the other blends. The lowest improvements were found with the melamine resin blends. It is seen that the substitution of as little as one part of epoxy resin by one part of DMEU produces an immediate increase of 25° in the crease recovery angle. The crease resistance of the higher ratios of epoxy/DMEU such as 7/3, 6/4, and 5/5 ranged from 270° to 275°. These values cannot be obtained by epoxy resins alone except at concentrations of over 20% solids.

Since these results indicated the superior performance of the epoxy/DMEU finishes, it was next necessary to determine the durability of such blended finishes as compared to that of the all-epoxy resin. In Figure 2 are shown crease resistance tests initially and after two launderings at the boil using mild soap and soda ash. These results show that only in the case of epoxy/DMEU blends was the crease resistance as durable to these strenuous washes.

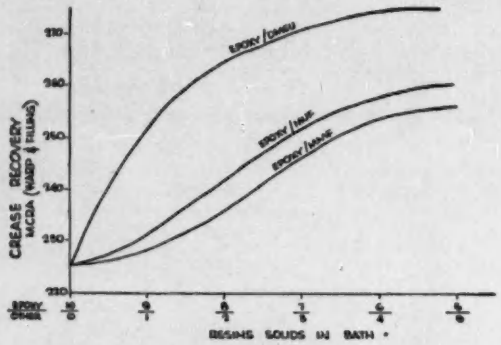


Fig. 1. Effect of epoxy blend ratio with nitrogenous resins on the crease recovery of 80 × 80 cotton fabric.

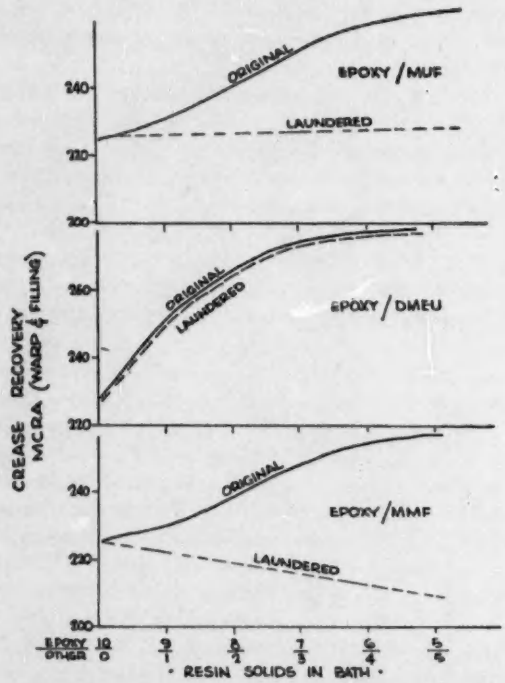


Fig. 2. Effect of laundering (two FSW/Alk) on the crease recovery of epoxy blend treated 80 × 80 cotton fabric.

Of greater importance for white cotton fabric finishes was the chlorine damage resistance of the various blends. In the case of pure epoxy finishes, it had been demonstrated earlier that these did not show chlorine damage under any condition of testing. With the blends of epoxy/DMEU, it was found that none of them showed any chlorine damage if the standard AATCC test was performed on the finished fabrics. Only by hot chlorination tests, higher temperature scorching, repeated chlorinations, or the AATCC test performed on repeatedly laundered fabrics could differences among the various samples be noted. In Figure 3 are shown the results of one such test. Here the DMEU, the methylated melamine, and the methylated urea formaldehyde resin treated controls all gave 100% loss in strength when tested by the AATCC procedure after the two highly alkaline boiling washes. The pure epoxy resin finished fabrics by this test all show less than 10% strength loss. Up to a ratio of 7/3 epoxy/DMEU, these blends appear to give the same complete protection against damage by chlorine bleaches as the pure epoxy resin. With the methylated urea and melamine resins, the blends begin to lose their chlorine damage resistance features at very low add-on of nitrogenous component in the blend. It should be noted that, with any of these blends, there is a safe region at low ratios of coreactant to epoxy where significant improvement in crease resistance but no chlorine damage occurs. Past this region, however, chlorine damage quickly begins to take place. Note the slope of the three curves as the amount of nitrogenous component increases.

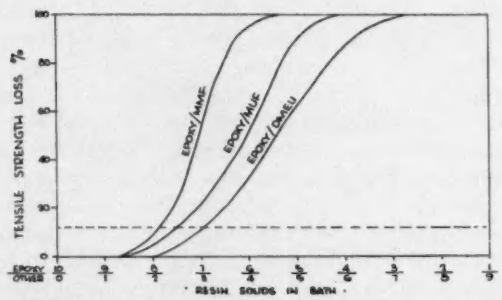


Fig. 3. Effect of two FSW/Alk launderings on the chlorine damage resistance (AATCC Tentative Test 69–1952) of epoxy blend treated 80 × 80 cotton fabric.

Since all three nitrogenous based coreactants, used alone at any of the concentrations given, generally show 100% strength loss under the laundering and chlorine test conditions used here, it would appear that the epoxy resin has minimized their chlorine retentive properties. There would seem to be no purpose, however, in using only small amounts of epoxy resin with these established creaseproofing agents, since the effect is not pronounced except at high concentrations of epoxy. The reverse is true, however, for crease resistance, where a small amount of DMEU added to the epoxy resin produces a remarkable improvement in crease recovery without lessening the protection against chlorine damage.

Under the test conditions of the FSW/Alk laundering followed by AATCC chlorine damage testing, DMEU, methylated methylol melamine, and methylated methylol urea resins charred completely when used alone. The untreated control, the epoxy control, and the 9/1 and 8/2 ratio of all blends produced no charring. Only with the epoxy/DMEU blends, however, do ratios as high as 5/5 in mild tests or 7/3 in more severe tests not produce any discoloration on ironing. With all three of the above nitrogenous resins at a 2/5 epoxy/coreactant ratio, the small amount of epoxy used lessens the scorching given by the other resins alone. This may be of some slight practical value with milder chlorine test performance requirements, but the use of low concentrations of epoxies to high concentrations of the nitrogenous resins is not recommended.

Comparison of Epoxy Blends with Other Resins

Since the blended finish based on seven parts of epoxy to three parts of dimethylol ethylene urea offered a good balance of cost, resistance to chlorine damage, and high crease resistance and wash-and-wear performance, further tests were made to compare this blend with straight epoxies and with other resins which have been used on white cotton fabrics. The bar graphs of Figure 4 show the initial crease resistance obtained with the various resin finishes at the solids content given. Also shown is the durability of crease resistance to three different types of laundering procedures: the two FSW/Alk washes at the boil with mild soap and soda ash, 20 home launderings, and 20 home launderings in the presence of chlorine bleach, as described earlier.

In examining these results, it is seen that the greatest durability was found with the 15% epoxy resin used alone. The next best durability to all washes was found with the 10% solids of the blend of 7/3 epoxy/DMEU. Note also the extreme durability of these two epoxy based finishes to multiple hot chlorine washes compared to the DMEU and triazone resins. The latter two had lost most of their original crease resistance after the 20 chlorine washes.

Of the three nitrogenous resins used alone, the modified methylated melamine showed the greater durability to the three washes. While this produced good durability even to the 20 hot chlorine washes,

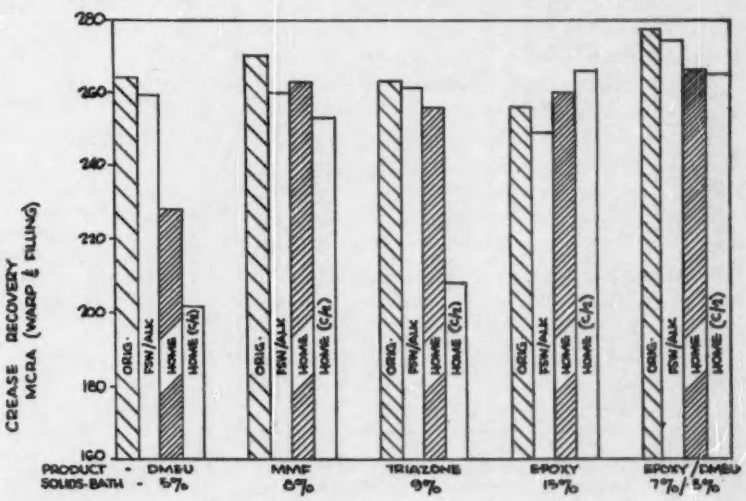


Fig. 4. Effect of type of laundering on the crease recovery of resin treated 80 × 80 cotton fabric.

the samples became progressively more yellow after the fifth wash cycle.

In Figure 5 are shown the results of the AATCC chlorine test performed on the samples after they had been given two FSW/Alk washes. Here it is seen that the epoxy resin, the epoxy/DMEU blend, the triazone, and the methylated melamine all showed high resistance to chlorine damage, although the melamine treated sample was discolored. The DMEU and a methylated urea-formaldehyde resin produced 100% loss in strength. Compare these results, however, with those obtained on the same samples after 20 hot chlorine soap washes, as shown in Figure 6. Here the epoxy and the epoxy/DMEU blend behaved the same as the untreated cotton. Higher strength losses were found with the DMEU and triazone, and complete strength loss was found in the melamine and the methylated urea resin treated samples.

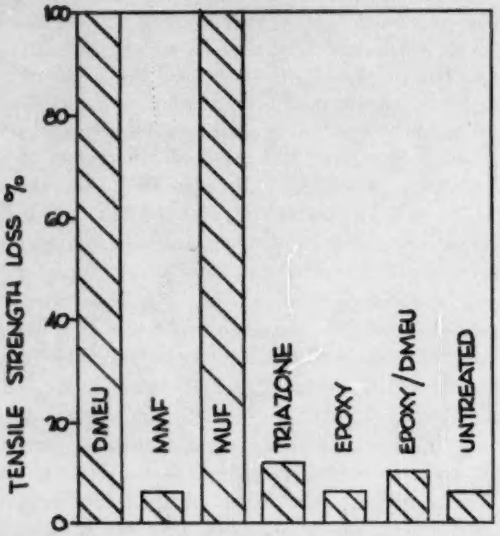


Fig. 5. Effect of two FSW/Alk launderings on the chloline damage resistance (AATCC Tentative Test 69-1952) of resin treated 80 × 80 cotton fabric.

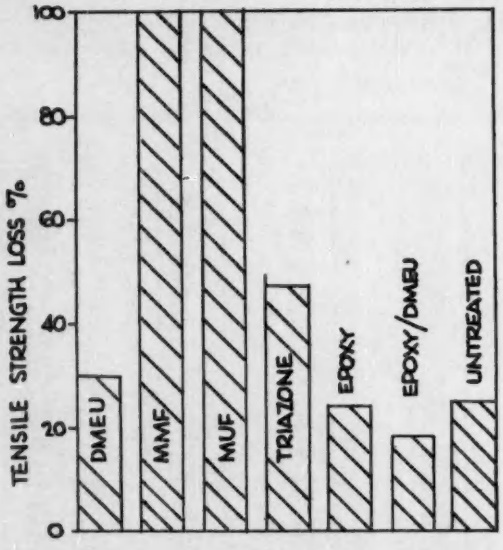


Fig. 6. Effect of 20 home launderings (soap/chlorine) on the tensile strength of resin treated 80 × 80 cotton fabric.

These results confirm other observations that while the nitrogenous based resins may appear to give good resistance to chlorine bleaches under selected test conditions, the epoxy resins alone or in combination with the DMEU are foolproof under most conditions of chlorination and scorching. This is true not only for tensile strength damage but also for durability of crease resistance and wash-and-wear properties.

Blends of Other Epoxy Resins

Since all of the above data was obtained by using only one epoxy resin (Eponite 100), studies were made of DMEU blends with other epoxy compounds. In this case, a second water soluble diepoxide (D-1), a monomeric diglycidyl ether of Bis Phenol A (Bis AI), and a polymeric Bis Phenol A epoxide (Bis AII) were used. These epoxies were used alone and in the blend of 7/3 epoxy/DMEU at 10% solids. The results are shown in Table VII.

TABLE VII. Blends of DMEU with Various Epoxies

Resin blend, epoxy/DMEU solids	MCRA (W+F)		Tensile strength, W×F, lb.
	Original	Laundered	Original
15% Eponite 100/0%	256	249	31×24
15% D-1/0%	260	261	32×22
15% Bis AI/0%	178	177	18×14
15% Bis AII/0%	178	178	30×18
7% Eponite 100/3%	277	274	28×22
7% D-1/3%	256	265	32×25
7% Bis AI/3%	246	257	28×24
7% Bis AII/3%	256	245	34×31
0% Epoxy/3%	229	223	42×38
Untreated control	160	157	56×45

When the epoxies were used alone, there was little difference between the performance of the Eponite 100 and the second diepoxide, both of which are water soluble essentially monomeric resins. No creaseproofing, however, was produced by either of the Bis Phenol A based resins, both of which are water insoluble and presumably not diffusible into the cotton fibers.

With the epoxy/DMEU combinations, at 10% total bath solids, the crease resistance obtained was as good or better than that of the 15% straight epoxies. Again, all of these finishes showed excellent durability to 20 home washings. It is noteworthy that while the Bis Phenol A based resins by themselves imparted no crease resistance, the combination of these same resins with the DMEU yielded high crease resistance, which can not be accounted for by the 3% DMEU alone.

In Table VIII are shown the results of chlorine damage resistance tests performed on these various epoxy/DMEU treated cotton fabrics. These illustrate the complete nonchlorine damaging feature of the all-epoxy finishes. With those water soluble epoxy resins which, by themselves, produce crease resistance, the blends with the DMEU do not show chlorine damage either before or after 20 home launderings. The Bis Phenol A based epoxies, however, when blended with the DMEU do not produce a chlorine damage resistant finish. These results strongly indicate that a specific reaction is involved in the soluble epoxy/DMEU blends, since comparable results are not obtained either with other epoxides or with the same epoxy and other nitrogenous resins.

TABLE VIII. Chlorine Resistance of Epoxy/DMEU Blends

Resin blend, epoxy/DME[1] solids	Warp tensile strength loss (AATCC 69–52), %	
	Original	Laundered
15% Eponite 100/0%	0	3
15% D-1/0%	0	9
15% Bis AI/0%	0	0
15% Bis AII/0%	0	0
7% Eponite 100/3%	0	10
7% D-1/3%	0	0
7% Bis AI/3%	0	100
7% Bis AII/3%	0	100
0% Epoxy/3%	3	100
Untreated control	3	4

TABLE IX. Catalyst Requirements with Epoxy/DMEU Blends

Resin blend, epoxy/DMEU solids, %	Zinc fluoborate in bath, %	MCRA (W+F)	Tensile strength, warp, lb.
10/2.5	1.0	240	32
10/2.5	1.5	255	29
10/2.5	2.0	266	29
8.25/4.25	1.0	251	31
8.25/4.25	1.5	272	29
8.25/4.25	2.0	273	27

Miscellaneous Studies of Epoxy Blends

The blends of epoxy resins with dimethylol ethylene urea have been commercially utilized for two years in producing wash-and-wear white cotton fabrics. As with other commercial processes, a host of variables have been investigated to obtain optimum performance.

In regards to catalysis, as with the straight epoxies, we have found that best results are obtained with zinc fluoborate as catalyst. There are very few other catalysts available which can cure either the epoxy or the epoxy blends on cotton fabrics. Limited success has been had with these blends by using the various alums, zinc sulfate, and magnesium perchlorate. The normal epoxy catalysts used in nontextile operations, such as the various polyamines and dibasic acid anhydrides, are entirely unsatisfactory for the curing of epoxies on cotton for crease resistant finishes.

Table IX shows the influence of catalyst concentration in curing two different epoxy/DMEU blends at 12.5% pad bath solids. These results confirm previous results with the straight epoxies and show that similar concentrations of zinc fluoborate must be used with the blends for proper curing.

In regards to cloth preparation, it has been found that the epoxy/DMEU blends are slightly less sensitive to the presence of alkalis on the cloth than are the straight epoxies. Nevertheless, optimum results can be obtained only in fabrics having low alkalinity, i.e., 0.05% or less.

It has been established that normal drying and curing conditions suitable for other resin finishes are satisfactory for the epoxy/DMEU blends. The best whites and best controlled hand and other properties are obtained when the treated fabrics are afterwashed with sodium perborate and a nonionic detergent. In cases where the afterwashing has been omitted, selected optical bleaches added to the treating bath produced a good white.

As with other resin finishes, considerable variation in hand and wash-and-wear properties can be obtained with the epoxy/DMEU blends by utilizing selected additives. These include a nonsoiling silicone softener, polyethylene, epoxidized soy bean oil, polyvinyl alcohol, polyvinyl acetate, and elastomeric latices. As with the straight epoxies, it is important not to use additives which will adversely affect chlorine damage resistance properties.

In cases where desirable additives are not compatible with the epoxy/DMEU blend, some of these can be applied as a top finish to alter the hand or mechanical properties. This is shown in Table X.

TABLE X. Top Finishing Epoxy/DMEU Treated Cottons With an Elastomeric Acrylic Latex

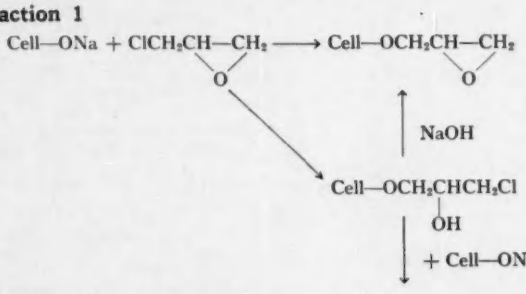
Fabric	Treatment	MCRA (W+F)	Grab tensile, filling, lb.	Elmendorf tear, fill, g.
136×60 Broadcloth	Unfinished	172	34	1070
	Finished epoxy/DMEU	264	23	480
	Finished + aftertreated	274	25	460
80×80 Print cloth	Unfinished	172	54	780
	Finished epoxy/DMEU	273	34	340
	Finished + aftertreated	289	34	300
Combed sateen	Unfinished	205	77	1600
	Finished epoxy/DMEU	279	54	1020
	Finished + aftertreated	284	56	1070

Review

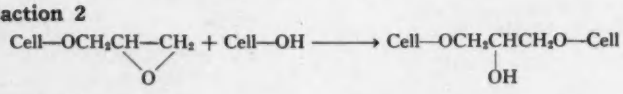
A broad study of the utility of blends of water soluble epoxy resins with other reactive chemicals has indicated that unusual cotton finishing effects may be obtained in some cases. So far, the use of blends of epoxies with dimethylol ethylene urea has produced finishing results not obtainable with either resin alone. These include essentially complete resistance to damage by chlorine bleaching, high crease resistance, wash-and-wear performance, and durability to repeated chlorine and other type launderings.

The search for other more efficient epoxides to be used alone or in blends with dialdehyde, DMEU, and other chemicals is continuing with particular effort to find even more economical and more efficient epoxy systems. Good possibilities exist also in the

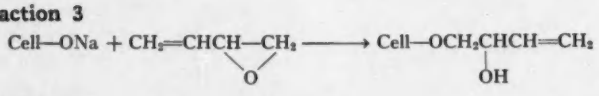
Reaction 1



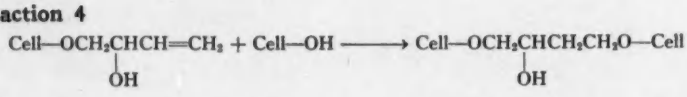
Reaction 2



Reaction 3



Reaction 4



explorations of the intermediates or precursors of epoxy resins which may be reacted with cotton. This includes epoxy alkenes and epichlorohydrin. Dreyfus [2], Musser [7], and Maxwell [6] have demonstrated the reaction of such epoxy compounds with cellulose to give simple monoethers and other derivatives. By a second reaction, these monoepoxy cellulose derivatives could be converted to cross-linked products. This is demonstrated below. In Reaction 1, cellulose reacts with epichlorohydrin to form the monoglycidyl ether, as an unstable intermediate, or to form the chlorohydrin ether, depending on reaction conditions. The chlorohydrin derivative, by dehydrohalogenation, can also be converted to the glycidyl ether. In Reaction 2, under acidic conditions, the glycidyl cellulose ether can react with other cellulose hydroxy groups to form the cross-linked product. Through an analogous two-step process, an epoxy butene could also be used to form a cross-linked cellulose (Reactions 3 and 4). While these reactions are listed separately, it may be possible under selected conditions to obtain direct cross-linking of the cotton cellulose in a one-step process either with epichlorohydrin, the epoxybutene, or other halohydrins.

There are other possibilities in devising cotton finishing treatments based on epoxy compounds. While many of these offer technical and economic complications, the whole family of epoxides is of great interest for textile finishing since, whenever reaction with the cellulose fiber occurs, the finishing effects can be expected to be permanent because of the high chemical stability of the bonds formed with the fiber polymer.

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Effect of Creaseproofing Agents on Lightfastness of Sensitive Dyes[1]

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Abstract

The lightfastness of several classes of dye is known to be greatly affected by certain types of finishing agents such as cationic softeners and conventional types of creaseproofing agents. However, little or nothing has heretofore been published by either the dye companies or chemical manufacturers regarding the effects on lightfastness of some of the newer or lesser known creaseproofing compounds.

Three classes of dye which show the greatest sensitivity of lightfastness are the directs, the diazotized and developed, and the new "linkage" or "reactive" type dyes. This paper will describe the effects on lightfastness of most of the presently available creaseproofing agents on these three classes of dyes. A few selected vat dyes will also be included in the study.

The data presented will be helpful to mills in selecting creaseproofing compounds for the finishing of dyed and printed fabrics.

Historical

Because of the very important advantages which can be imparted to textiles through the use of creaseproofing agents, there has been a tendency to overlook some of the disadvantages which occur simultaneously. The possible adverse effect which some of these agents have on lightfastness is one of the more important properties which is often disregarded by the chemical manufacturers and neglected by the finishing plants.

Considerable effort has been spent in the last five to ten years by certain individuals and groups to close this gap in our knowledge concerning certain of these agents.

Particularly noteworthy work has been done in this country by AATCC Intersectional Contest Committees [1, 2, 3, 7]. As examples, the Rhode Island Section studied the effect on lightfastness of direct dyes when aftertreated with urea formaldehyde resins. Secondly, the Piedmont Section studied the effects of dimethylol cyclic ethylene urea and methylol melamine on the lightfastness of vat dyes. Most recently, the Piedmont Section continued its study on vat dyes and has included certain other resins such as methylated trimethylol melamine, acetone formaldehyde, acrolein formaldehyde, epoxy, and formaldehyde hydantoin resins. During this period, Landolt [5] studied the specialized effects of acid colloids, and Polito [6] studied treatments on acetate dyeings.

The recent introduction of fiber reactant dyes [9], which are an entirely new class of dye, focused our attention on this problem. We decided to check the effect of our various resins on the lightfastness of these dyes; at the same time, we decided to include representative members of some other classes of dye which were known to be sensitive to the effect of resins. Finally, we included all resins of commercial importance which are manufactured by others and which represent types of resins which we do not presently manufacture. This paper summarizes the results of that study.

Experimental

Dyes Studied

Fiber reactant dyes were the primary object of our investigation; therefore we included the complete line, as shown in Table I. A black has recently been introduced, but is not included because it wasn't available when this work started.

[1] Presented at the 7th Chemical Finishing Conference, National Cotton Council, Washington, D. C., October 1, 1958.

No Color Index or Prototype numbers are given in Table I because the fiber reactant dyes are so new that they haven't yet been classified.

The fiber reactant dyes were applied by the pad-dry-chemical pad-steam method. This involved padding the goods through a solution containing 1.5 g./l. of the dye plus 2 g./l. of a nonionic wetting agent. The goods were dried in an air-flue type lab drier. Then they were padded with a solution containing 1% caustic soda plus 30% common salt. The goods were then steamed in a laboratory steamer for 15–60 sec. at 160° C. This was followed by very thorough soaping and rinsing in a beaker.

Five widely used diazotized and developed colors were included with two different developers. These are listed in Table II.

Dyeings (1%) were applied in a bucket using a 40:1 bath:fabric ratio. After the fabric was thoroughly wet out, the predissolved dye was added at 120° F. and the bath brought to the boil. Common salt (1%) was added and the bath held at the boil for 15 min. The fabric was then rinsed with cold water and then diozatized at room temperature with 2% sodium nitrite plus 3% concentrated hydrochloric acid. After the fabric was rinsed with cold water, the color was developed by adding 1% of the predissolved developer (using caustic soda to dissolve) and then running at room temperature for 20 min. The fabrics were then rinsed cold, soaped hot, and finally rinsed thoroughly.

Three special vat colors were selected for this study. These were the colors which previous workers [1, 2] in this field had shown to be the most sensitive. A listing of these three dyes and the materials used in the dyeings is given in Table III.

The dyeing procedure was to prepare the bath in a pot at a 40:1 bath:fabric ratio by adding the vat pigment dispersion, Albatex POK, and the caustic soda at 120° F. Enter the wetted-out fabric and dye for 5 min. Add ½ the amount of hydro and dye for 5 min. Add the remaining half of the hydro and dye for 30 min. Rinse cold with a small amount of hydro. Oxidize with 2% sodium perborate at

TABLE I. Fiber Reactant Dyes

Procion blue 3G
Procion brilliant blue H7G
Procion brilliant blue R
Procion brilliant orange G
Procion red 5B
Procion red G
Procion rubine B
Procion brilliant yellow 6G
Procion yellow R

TABLE II. Diazotized and Developed Colors

Dye	Color index or prototype	Developer
Diazo red 7BL	PR. 85	β Naphthol
Pontamine diazo blue BR	PR. 74	α Naphthol
Pontamine diazo bordeaux 2BL	PR. 172	α Naphthol
Pontamine diazo green BL	—	Developer ZN
Pontamine diazo yellow 2 GL	—	Developer ZN

TABLE III. Vat Dyes

	Cibanone golden orange 3G (PR. 290)	Cibanone golden orange 2R (C.I. 1098)	Cibanone red F BB (PR. 296)
Amount of dye	0.5%	0.5%	0.3%
Albatex POK	0.1%	0.1%	0.1%
Caustic soda, 66TW	4 cc./l.	15 cc./l.	4 cc./l.
Hydro	0.2%	0.6%	0.2%

TABLE IV. Fast-to-Light Direct Colors

Dye	Color index or prototype
Fastusol blue LRRU	PR 613
Fastusol brilliant blue L8GU	PR 432
Fastusol orange L8GL–CF	—
Fastusol red L4BL–CF	PR 428
Fastusol yellow LEFC–CF	PR 629

TABLE V. Urea Formaldehyde Resin Treatments

Type resin	Urea : formaldehyde ratio	Catalyst	Treatment code
Methylol urea	1.0 : 1.3	Amine hydrochloride	U.F.(1.0 : 1.3)-AM
Methylol urea	1.0 : 1.3	Magnesium chloride	U.F.(1.0 : 1.3)-MGCL
Methylol urea	1.0 : 2.0	Amine hydrochloride	U.F.(1 : 2)-AM
Methylol urea	1.0 : 2.0	Magnesium chloride	U.F.(1 : 2)-MGCL
Methylated U.F.	1.0 : 2.0	Amine hydrochloride	M.U.F.(1 : 2)-AM
Methylated U.F.	1.0 : 2.0	Magnesium chlorine	M.U.F.(1 : 2)-MGCL

120° F. for 15 min. Rinse, soap with neutral detergent for 10 min. at the boil, and then rinse cold.

Five commonly used fast-to-light directs were included; these are listed in Table IV. These direct dyes were applied in a pot, using a 20:1 bath:fabric ratio. The goods were thoroughly wet out using 0.5% of Igepon T-51. The dye was predissolved in boiling water and then added to the bath at 100° F. Raise temperature to 160° F. and then add 20% common salt. Raise temperature to the boil and boil for 45 min. Allow to cool for 15 min., and then rinse cold until clear.

In all cases, the dyeings were made on mercerized and bleached 80 × 80 cotton print cloth. Although many of these dyes are also used on viscose, we didn't include viscose dyeings in this study in order to minimize the number of fading exposures. Furthermore, past studies [4, 7] have shown that results on cotton and viscose are generally comparable.

TABLE VI. Cyclic Ethylene Urea Treatments

Type resin	Free formaldehyde, %	Catalyst	Treatment code
Dimethylol C.E.U.	0.5	Magnesium chloride	C.E.U.-0.5-MGCL
Dimethylol C.E.U.	2.6	Magnesium chloride	C.E.U.-2.6-MGCL
Dimethylol C.E.U.	2.6	Cupric chloride	C.E.U.-2.6-CUCL

TABLE VII. Miscellaneous Nitrogenous-Formaldehyde Resin Treatments

Type resin	Catalyst	Treatment code
Dimethylol triazone	Salt complex	Triazone
Experimental dimethylol cyclic	Buffered acid	Cyclic-exp
Tri-substituted melamine	Magnesium chloride	Tri-mel
Hexa-substituted melamine	Magnesium chloride	Hexa-mel
Guanyl urea—formaldehyde	Amine hydrochloride	Guanyl
Tetramethylol acetylene diurea	Magnesium hydrochloride	T.A.D.U.
Epoxy—C.E.U. combination	Zinc fluoborate	Epoxy—CEU

TABLE VIII. Non-Nitrogenous Treatments

Type resin	Catalyst	Treatment code
Ketone—formaldehyde	Caustic soda	K.A.
Epoxy	Zinc fluoborate	Epoxy

Resins Studied

For convenience in this paper we use the word "resin" loosely to include not only the true resin-forming compounds but also the monomeric fiber reactant type treatments. To simplify presentation we have divided the resins into four group.

Table V lists the urea formaldehyde resins. Included in this series we have methylol urea products at two different urea formaldehyde ratios. Also, the methylated urea formaldehyde type is included. Table VI deals with dimethylol cyclic ethylene urea at two levels of free formaldehyde. Table VII lists a variety of nitrogenous-formaldehyde type resins. Table VIII lists the non-nitrogenous treatments which were included. As can be seen from the tables, we also varied the catalyst to determine what effect, if any, was due to the catalyst. Table IX lists the commercial names of the various resins and catalysts used.

Table X summarizes the actual treatments, giving the pad bath composition as well as the code designations for the treatments.

Application of the resin treatments to the dyed fabrics was the same in all cases and was as follows. The dyed fabrics were soured in 1% acetic acid, rinsed thoroughly, and then dried. The resin baths were made up as indicated in Table X, following the manufacturer's instructions for mixing. The dyed fabrics were impregnated in a two-roll laboratory padder, using 2 dips and 2 nips to provide approximately 70% wet pick up. The fabrics were then dried for 2 min. at 250° F. and then cured for 2 min. at 320° F. in a forced circulation curing oven. After curing, the triazone, epoxy, epoxy-C.E.U., and the ketone aldehyde finished fabrics were afterwashed. The other treatments weren't afterwashed because it is common mill practice not to afterwash these types.

Lightfastness Testing and Method of Rating

All treated fabrics were exposed for 10 and 20 hr. in a Fade-Ometer, Type FDA-R. We did not run sunlight exposures; sufficient data have already been accumulated by others [1, 4, 7] to indicate a close correlation between sunlight exposure and the Fade-Ometer.

After exposure, the dyed fabrics were rated for the degree of fading. For our standard, we used the Geometric Grey Scale as supplied by The Society of Dyers and Colourists. The fastness rating of the specimen is that number of the Grey Scale which corresponds to the contrast between the exposed and the unexposed areas. Although some of the resin treatments caused a change in shade as compared to the original dyeing, this effect was disregarded in our fastness ratings. Each specimen was rated indi-

TABLE IX. Commercial Products Used

Type resin or catalyst	Trade name	Manufacturer
Methylol urea (1.0 : 1.3)	Formaset SN	Warwick Chemical Div.
Methylol urea (1 : 2)	Lab preparation	—
Methylated U.F.	Permafresh 424	Warwick Chemical Div.
Dimethylol CEU (2.6% free form.)	Permafresh E	Warwick Chemical Div.
Dimethylol CEU (0.5% free form.)	Lab preparation	—
Dimethylol triazone	Permafresh LCR	Warwick Chemical Div.
Experimental dimethylol cyclic	Pilot plant prep'n	Warwick Chemical Div.
Tri-substituted melamine	Aerotex M-3	American Cyanamid
Hexa-substituted melamine	Aerotex 23 Special	American Cyanamid
Guanyl urea-formaldehyde	Warcofix 403	Warwick Chemical Div.
Tetramethylol acetylene diurea		Onyx
Epoxy	Eponite 100	Shell
Ketone formaldehyde	Prym KA	Warwick Chemical Div.
Amine hydrochloride	Permafresh Catalyst 376	Warwick Chemical Div.
Salt complex	Permafresh Catalyst LXX	Warwick Chemical Div.
Buffered acid	Permafresh Catalyst W	Warwick Chemical Div.
Zinc fluoborate	Catalyst C-42	Rohm and Haas
Emulsifier	Rhotex A-9	Rohm and Haas

TABLE X. Summary of Treatments (Pad Bath Composition)

Treatment code	Pad bath composition
U.F. (1.0 : 1.3)–AM	30% Formaset SN 1.5% Catalyst 376
U.F. (1.0 : 1.3)–MGCL	30% Formaset SN 3% $MgCl_2 \cdot 6H_2O$
U.F. (1 : 2)–AM	30% Dimethylol urea paste (60% solids) 1.5% Catalyst 376
U.F. (1 : 2)–MGCL	30% Dimethylol urea paste (60% solids) 3% $MgCl_2 \cdot 6H_2O$
M.U.F. (1 : 2)–AM	15% Permafresh 424 1.8% Catalyst 376
M.U.F. (1 : 2)–MGCL	15% Permafresh 424 3% $MgCl_2 \cdot 6H_2O$
C.E.U.–0.5–MGCL	15% Dimethylol CEU (with 0.5% freeform) 3% $MgCl_2 \cdot 6H_2O$
C.E.U.–2.6–MGCL	15% Permafresh E 3% $MgCl_2 \cdot 6H_2O$
C.E.U.–2.6–CUCL	15% Permafresh E 2% $CuCl_2$
Triazone	20% Permafresh LCR 2.4% Permafresh Catalyst LXX
Cyclic–exp.	15% Experimental dimethylol cyclic 3% Permafresh Catalyst W
Tri–mel	10% Aerotex M-3 3% $MgCl_2 \cdot 6H_2O$
Hexa–mel	12% Aerotex 23 Special 3% $MgCl_2 \cdot 6H_2O$
Guanyl	4% Warcofix 403 0.4% Catalyst 376
TADU	15% Tetramethylol acetylene diurea (50% solids) 3% $MgCl_2 \cdot 6H_2O$
Epoxy–CEU	9.0% Eponite 100 7.5% Permafresh E 2.5% Rhotex A-9 1.5% Catalyst C-42
K.A.	20% Permafresh KA 1% NaOH
Epoxy	12.5% Eponite 100 2.5% Rhotex A-9 1.5% Catalyst C-42
Untr.	Distilled water only

vidually by four members of a panel; the average of the four ratings was recorded as the fastness rating of the specimen.

A qualitative description of the fastness ratings is given in Table XI.

Results

Tables XII, XIII, XIV, and XV summarize the fastness ratings of the various dyeings and treatments after 20 hr. of exposure.

Discussion of Results

With regard to urea based resins, the ratio of urea to formaldehyde seems to have little or no effect on the degree of fading. This does not agree with the findings of the Rhode Island Section [3]; they found that dimethylol urea caused much more fading than monomethylol urea. We feel that the explanation for this discrepancy may be due to the fact that they chose a 1:1 ratio as their lower limit, whereas we chose the ratio of 1:1.3, which is about the lowest formaldehyde content that is commercially acceptable. Using a 1:1 ratio gives no resin formation, essentially no crease resistance, and could very well have resulted a misleading effect on lightfastness.

Referring further to urea formaldehyde resins, we found that the bis (methoxymethyl) derivative gave essentially the same effect on lightfastness as does the dimethylol derivative. This clearly indicates that the presence of methylol groups is not essential to cause fading, as was originally proposed by the Piedmont Section.

At least on the basis of the catalysts included in this study, there is good evidence to indicate that the choice of the catalyst can have an important effect on the degree of fading. So much so, in fact, that in some cases a change in the catalyst caused a more pronounced effect on lightfastness than did the urea:formaldehyde ratio or other changes in the resin. However, it is well to keep in mind that many of these treatments were not afterwashed. Thus, any detrimental effect attributable to catalyst is probably of a transitory nature, and it is likely that such effects will be eliminated after the fabric has been laundered.

As to the melamine products included in this study, it appears that the hexa-substituted product causes slightly more adverse effect on lightfastness

TABLE XI. Rating Scale

Fastness rating	Description
5	No change
4	Slight change
3	Appreciable change
2	Considerable change
1	Very great change

TABLE XII. Fastness Ratings of Fiber Reactant Dyes

Treatment	Blue 3G	Brill. blue H7G	Brill. blue R	Brill. orange G	Red 5B	Red G	Rubine B	Brill. yellow 6G	Yellow R	Average
U.F. (1.0 : 1.3)AM	4.3	2.5	4.3	4	2.3	4.5	5	4	5	4
U.F. (1.0 : 1.3)MGCL	4.7	4.4	5	4.7	4.5	5	5	5	4.5	4.7
U.F. (1 : 2)AM	4.5	3.7	4	3.5	1.9	3.3	4.5	4	5	3.8
U.F. (1 : 2)MGCL	4.7	3.5	4.7	4.5	4	5	5	4.5	5	4.5
M.U.F. (1 : 2)AM	4.7	2.5	4.7	3.8	2.7	3.8	4.7	3.8	4.5	3.9
M.U.F. (1 : 2)MGCL	4.7	3.5	4.7	3.9	3.9	3.9	5	4	5	4.3
C.E.U.–0.5–MGCL	2.5	1.9	2.2	1.8	1	1.2	3.3	3.5	4	2.4
C.E.U.–2.6–MGCL	2.5	2	2.3	2.3	1.1	1.7	3	3.5	4.5	2.5
C.E.U.–2.6–CUCL	2.7	2	2.7	1.5	1.2	1.5	2.5	3	2	2.1
Triazone	4.3	2.5	3.5	2	1.4	1.9	3.8	3	4.5	3
Cyclic–exp.	4.7	3.5	4.7	4.5	3.5	4.7	4.7	4.5	3.5	4.3
Tri–mel	3.5	3.7	3.5	3	1.7	3	3.6	4	5	3.4
Hexa–mel	3	2.5	3.5	2.9	1.5	2	4.1	3.5	5	3.1
Guanyl	4	2.5	4.3	2.8	1.5	2.7	2.7	3.5	4	3.1
TADU	4.7	3.5	5	4.2	4.7	4	5	4.5	4.5	4.5
Epoxy–C.E.U.	4.3	2.5	4.3	2.8	1.6	2.4	4.1	3.5	3	3.2
KA	4.3	2.5	4.3	3.7	2.5	3.5	4.1	4	4	3.6
Epoxy	4.9	3.5	4.3	3	3.1	2.7	4.5	3	3.5	3.6
Untreated	4.8	3.8	4.9	2.0	3.5	3.7	5	4.5	4.8	4.3

than does the tri-substituted product. However, aside from this rating, it is unwise for us to attempt to postulate the reasons because we are uncertain of the actual chemical nature of the so-called hexa-substituted product.

With the dimethylol cyclic ethylene urea product, variation in the free formaldehyde content of the product didn't produce an appreciable effect on light-fastness. The product containing 2.6% free formaldehyde did show slightly less fading in some instances, but the difference is not sufficiently great to be of practical value.

While it is known that the presence of copper is often very beneficial to prevent the degradative effects on lightfastness caused by certain cationic resins, this study has shown that copper is of no value in counteracting the loss of lightfastness that occurs with cyclic ethylene ureas.

With the non-nitrogenous finishes, we found some increases in the amount of fading as compared to untreated dyeings. However, we don't have sufficient data at this time to be able to state whether the increased fading is due to the resin or to some other factor such as catalyst, yellowing of the resin, etc.

A relative ranking of the resins included in this study shows the following.

1. Without exception, dimethylol cyclic ethylene urea has the greatest adverse effect on lightfastness.

2. Guanyl urea-formaldehyde resin is next in it's effect on lightfastness. Other studies, not reported in this paper, have shown that the inclusion of copper compounds in such treatments substantially reduce the loss in lightfastness.

3. With still less effect on lightfastness, we find

TABLE XIV. Fastness Ratings of Vat Dyes

Treatment	Orange 2R	Orange 3G	Red FBB	Average
U.F. (1.0 : 1.3)AM	4.6	4.7	4	4.4
U.F. (1.0 : 1.3)MGCL	5	5	4.4	4.8
U.F. (1 : 2)AM	4.6	4.5	4.3	4.5
U.F. (1 : 2)MGCL	5	5	4.4	4.8
M.U.F. (1 : 2)AM	3.6	4.7	4.5	4.3
M.U.F. (1 : 2)MGCL	4.5	5	4.7	4.7
C.E.U.–0.5–MGCL	4.4	3.3	3	3.6
C.E.U.–2.6–MGCL	4.4	3.8	3.1	3.8
C.E.U.–2.6–CUCL	4.4	3	3.5	3.6
Triazone	3.7	4	4.3	4.0
Cyclic exp	4 5	4.8	4.7	4.7
Tri–mel	4.4	4	4.3	4.2
Hexa–mel	3.7	4	3.2	3.6
Guanyl	4	4.5	4.5	4.3
TADU	4.6	4.9	4.6	4.7
Epoxy–CEU	3	5	3.5	3.8
KA	4.7	5	4.1	4.6
Epoxy	3.3	4.7	3.4	3.8
Untreated	3.5	4.9	4.7	4.4

TABLE XIII. Fastness Ratings of Diazotized and Developed Colors

Treatment	Red 7BL	Blue BR	Bordeaux 2BL	Green BL	Yellow 2GL	Average
U.F. (1.0 : 1.3)AM	4.8	3.8	4.5	4.3	5	4.5
U.F. (1.0 : 1.3)MGCL	5	4.5	5	5	5	4.9
U.F. (1 : 2)AM	4.7	3.8	3.6	4	4.5	4.1
U.F. (1 : 2)MGCL	5	5	5	5	5	5
M.U.F. (1 : 2)AM	4	3.3	3.3	4	3.8	3.7
M.U.F. (1 : 2)MGCL	4.5	4.7	4	5	4.5	4.5
C.E.U.–0.5–MGCL	2.7	2.1	1.6	3.3	4	2.7
C.E.U.–2.6–MGCL	2.5	2.2	1.7	3.8	4	2.8
C.E.U.–2.6–CUCL	2	1.8	1.5	2	2	1.8
Triazone	3.0	2.5	2.7	3	3.3	2.9
Cyclic exp.	4.2	4.8	4.1	5.0	4.0	4.4
Tri–mel	3.4	3.3	2.7	4.3	4	3.5
Hexa–mel	3.5	3	3	4.3	3.8	3.5
Guanyl	2.4	2.8	1.9	3.4	3.5	2.8
TADU	4.5	4.8	4.5	4.5	4.3	4.5
Epoxy–CEU	3.3	3	2	4.1	3.5	3.2
KA	3.2	3.3	2.5	3.8	4.3	3.4
Epoxy	3.7	3.3	2.5	4.3	3.0	3.3
Untreated	3.2	4.0	2.5	4.5	3.5	3.5

a miscellaneous group of finishes: melamine formaldehyde resins, triazones, and non-nitrogenous finishes. While their effect is not severe, these finishes consistently cause some deterioration in lightfastness.

4. For creaseproofing treatments which have little or no adverse effect on lightfastness, we find a novel chlorine resistant dimethylol cyclic compound, urea formaldehyde resins, and tetramethylol acetylene diurea. In many instances, these compounds actually improve lightfastness as compared to the untreated dyeings. The fact that several of these compounds contain methylol groups further substantiates the conclusion that methylol groups do not cause fading *per se*. The dimethylol cyclic compound included in this group is a very recent development which has already been produced on a semi-works basis. Because of patent considerations, we are sorry that we are unable to describe the chemical structure. However, we would like to point out that this compound provides a very interesting and unique combination of properties; it is the only chlorine-resistant resin which has little or no effect on lightfastness.

The lightfastness of all four classes of dyes studied appears to be substantially affected by certain types of creaseproofing agents. What is very surprising is the uniformity with which all of the dyes react to the various treatments. Stated differently, the treatments which cause an adverse effect on lightfastness do so uniformly on all of the dyeings; those treatments which cause no adverse effects are uniformly good with all of the dyeings. To illustrate this point, we have selected one typical dye from each class and have shown graphically the effect on fading due to the various treatments. A comparison of the data shown in Figures 1–4 clearly demonstrates this remarkable uniformity. Although the degree of fading is not the same for the various dye classes, the relative effects of the various finishes is quite similar. Because of the great variety in the types of dyes used in this study, this leads us to the conclusion that the effect which these resins have on lightfastness is probably not due to a reaction between the resin and the dye. Instead, we feel that our data strengthen the view that these effects are due to some light screening phenomenon, such as radiation antagonism [2].

All experiments were performed on cloth dyed with a single color in each case. It has been our experience that a commercial dyeing, which usually involves a mixture of colors, will simply produce an additive effect of the individual colors present. Along these lines, some of the anomalies cited by Smith [8] may well have been due to poor control during his experimentation.

Summary

In selecting a resin to produce crease resistance or wash-wear properties, the finishing plant must

TABLE XV. Fastness Ratings of Fast-to-Light Directs

Treatment	Blue LRRU	Brill. blue L8GU	Orange L8GL–CF	Red L4BL–CF	Yellow LEFC–CF	Average
U.F. (1.0 : 1.3)AM	5	5	5	4.7	5	4.9
U.F. (1.0 : 1.3)MGCL	5	5	5	5	5	5
U.F. (1 : 2)AM	5	4.7	5	4.7	5	4.9
U.F. (1 : 2)MGCL	5	5	5	5	5	5
M.U.F. (1 : 2)AM	5	4.9	5	4.7	5	4.9
M.U.F. (1 : 2)MGCL	5	5	5	4.8	5	4.9
C.E.U.–0.5–MGCL	3	4.2	4.7	3.3	4.2	3.9
C.E.U.–2.6–MGCL	3	4.3	4.7	3.5	4.2	3.9
C.E.U.–2.6–CUCL	2.5	2.5	3	3	3.5	2.9
Triazone	4.5	4.5	4.2	3.5	4	4.1
Cyclic–exp.	5	5	5	5	5	5
Tri–mel	4	4.5	5	4	4.5	4.4
Hexa–mel	4.2	4.9	4.8	4.0	4.7	4.5
Guanyl	3.5	4.5	4.7	3.7	4.3	4.1
TADU	5	5	5	5	5	5
Epoxy–CEU	4.5	4.5	4.2	4.2	4.5	4.4
KA	5	4.7	4	3.8	4.7	4.4
Epoxy	5	4.5	4	4.5	4.7	4.5
Untreated	5	4.7	4.8	4.9	5	4.9

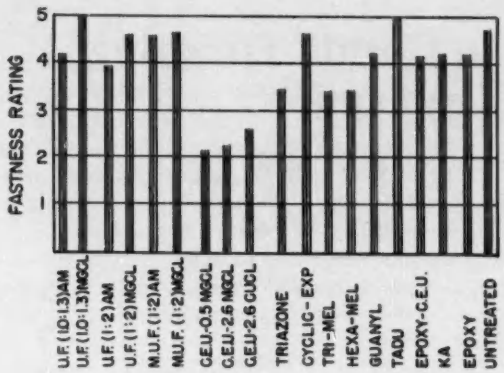

Fig. 1. Procion brilliant blue R (fiber reactant).

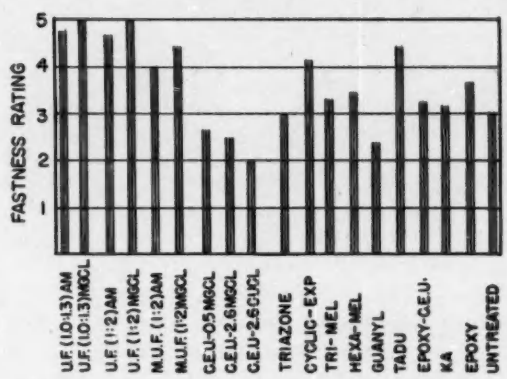

Fig. 2. Diazo red 7BL (diazotized and developed).

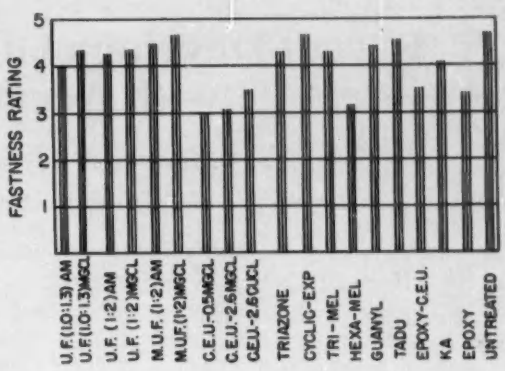

Fig. 3. Cibanone red FBB (vat).

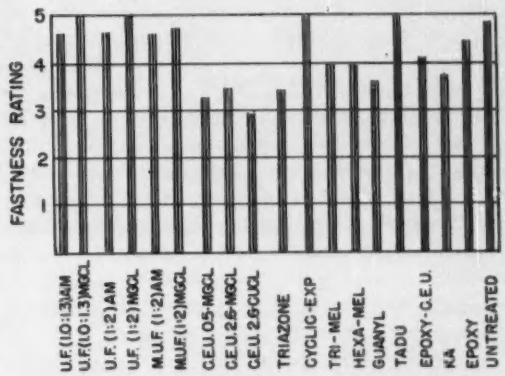

Fig. 4. Fastusol red L4BL-CF (fast-to-light direct).

choose a resin which will fulfill, to the desired extent, certain requirements such as chlorine resistance, permanency of finish, wet soiling properties, utility in mechanical finishing operations, and so forth. For dyed and printed fabrics, the effect which the finish may have on the lightfastness of the dyes must also be considered.

We have presented data which show the effect of a number of commercial creaseproofing treatments on the lightfastness of four classes of sensitive dyes. We hope that this information will be found helpful to the finishing plants in the selection of creaseproofing treatments.

Acknowledgment

We wish to thank Mr. Herb Kilgus of Cranston Print Works, Mr. E. C. Collins of General Dyestuff Co., Mr. Don Eccleston of Arnold Hoffman Co., and Mr. Fernand Schlaeppi of Ciba Co. for supplying the various dyed fabrics used in this work.

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Recent Developments in Cotton Finishing with Acetal Reactants[1]

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Abstract

An acetal cellulose reactant which imparts high crease resistance to fabrics is discussed. Determination of optimum conditions of application in the laboratory are followed by discussion of several applications in textile mills.

A catalyst which permits low temperature rapid curing of acetal reactants is also discussed. Results of textile mill usage of the catalyst are given.

An efficiency factor relating crease resistance increase to tensile loss is suggested.

Introduction

Acetal reactants are relatively new entrants in the field of cellulosic fiber modification. Their practical applications to cotton fabrics for dimensional stabilization and crease resistance were first discussed in detail at the Sixth Annual Chemical Finishing Conference of the National Cotton Council [1]. Since that time much progress has been made toward developing a wider range of improved fabric properties by treatment with newer acetal reactants.

A significant development during the past year has been the introduction of a new modification of the glycol acetals for wash-wear finishing of cotton. This product, now known as Quaker Reactant 53®, is closely related to the Quaker Reactant 16 which was discussed at the previous meeting. It will be the principal object of this paper to discuss textile mill applications of this latest acetal reactant to various cotton fabrics.

Review of Recent Finishing With the Earlier Modified Glycol Acetal

It is appropriate to review briefly recent progress in the use of the earlier glycol acetal, Quaker Reactant 16, which has found steadily expanding commercial use on woven fabrics because of its ability to exert chlorine safe dimensional control at very low tensile loss. The low tensile loss probably results in part from the relatively gentle cures which have been found to be satisfactory for use on this type of acetal reactant. The product can be cured in less than 60 sec. at normal curing temperatures (315–340° F.) or it can be cured with normal curing times (60–120 sec.) at temperatures near 300° F. Another factor favorable to the use of this early modified glycol acetal is the fact that it does not require an afterwash. Three examples of typical production uses follow.

The usefulness of this product on a fabric known to have very little to spare in tensile strength is shown in Table I. This also presents an example of the very gentle curing previously mentioned. Note the total of 30 sec. cure time, the first 20 of which were done at 260° F.

At a cost of only 1½ lb. in the filling and 6 lb. in the warp, this fabric has been processed to give satisfactory dimensional control.

The reduction in compression at the Sanforizer resulted in a 5.6% yardage saving, which offset the cost of processing.

Corresponding efforts to produce the same effect with a dimethylol ethylene urea were hampered by the necessity for undercuring to preserve tensile strength. This undercuring led to less effective dimensional control, to less saving at the Sanforizer, and to greatly increased susceptibility to chlorine damage.

The treatment and evaluation of sport denim (Table II) presents another example of shrinkage control with very low tensile loss as well as another example of quick curing. The fabric was cured 30 sec. at 320° F.; the loss in tensile strength was only 3 lb. in the filling and zero in the warp.

[1] Presented at the Chemical Finishing Conference of the National Cotton Council, Washington, D. C., October 2, 1958.

The increased fabric yield of 6½% was accompanied by dead set shrinkage control. Chlorine retention was of no importance on this fabric, and therefore was not measured.

A mildly springy, crisp finish was required, so the fact that the early modified glycol acetal does not produce high crease resistance was no hindrance to satisfactory production of the fabric.

The processing of a 5000-yd. lot of fabric treated with the acetal reactant to obtain *increased yardage yield* was very carefully followed by a mill accountant. The findings of that part of the investigation are listed in the first block of data under Evaluation (Table III).

This actual measurement substantiated the 3% yardage gain which had been calculated as the difference between the percent Sanforizer compression necessary with untreated fabric and that required for the reactant-treated goods. Part of the 15% reduction in warp tensile strength was caused by the fact that the finished fabric was pulled out wider than the prepared fabric, thereby slightly reducing the number of ends clamped in the subsequent break tests.

The apparent rise in filling strength also resulted from a mechanical shift. In the prepared state this fabric was stretched about 6% over greige length. After chemical treatment and the subsequent compressional shrinkage, the filling yarns were again closer to each other, thus causing a larger number of yarns to be clamped and broken in each break test.

The shrinkage control of this lot was slightly better than that of the usual production of that particular fabric.

Here again, shrinkage control was coupled with very low tensile change. At the same time, increased fabric yield has been confirmed by measurement.

TABLE I. Cotton Flannel

Formula	Processing
7.5% Modified glycol acetal	Padded at 65% wet pick-up
2.5% Magnesium chloride catalyst*	Dried on cans
2.0% Fatty softener	Cured—20 sec. at 260° F. plus 10 sec. at 330° F.
0.5% Wetting agent	Sanforizer compressed
	Not afterwashed

* Aerotex Accelerator MX

Evaluation		Untreated	Acetal treated	DMEU treated
Tensile strength, lb.		29 × 18	23 × 16½	
Percent shrinkage in 1 hr.; launderings at 212° F.	1 wash		0.1	1.1
	5 washes		0.8	1.7
	10 washes		1.6	
Removed at Sanforizer		8.9%	3.3%	6.4%
Saved			5.6%	2.5%
Chlorine damage	1 wash	0	9%	71%
	5 washes	0	6%	71%

Development of a New Glycol Acetal

The general usefulness of this first modified glycol acetal suggested the possibility of a product with similar advantages, with the additional quality of high crease resistance. Research and development with this combination of properties as the objective led to a new glycol acetal, which is to be discussed here.

Chlorine safety, durability of effect, ease of curing, and high crease resistance were all obtained. However, in order to obtain an acetal which would impart high crease resistance, it was necessary to give up the property of exceptionally low tensile loss.

Patent applications covering these modified glycol acetals are pending.

Efficiency of Crease Resistance Treatments

A most important relation among the practical considerations of processing cotton fabrics to obtain crease resistance is the question of how much tensile loss is to be sacrificed to obtain a given crease resistance increase. This can be expressed as a simple

TABLE II. Sport Denim

Formula	Processing
10.0% Modified glycol acetal	Padded at 65% wet pick-up
2.5% Magnesium chloride catalyst	Dried on cans
	Cured 30 sec. at 320° F.
3.0% Fatty softener	Sanforizer compressed
2.0% Starch ether	Not afterwashed
0.5% Wetting agent	

Evaluation		Untreated	Treated
Tensile strength, lb.		116 × 46	116 × 43
Fabric yield, %	Removed at Sanforizer	12.1	5.6
	Saved		6.5
Shrinkage, %	5 washes at 212° F.	0.6	+0.7
	10 washes at 212° F.	1.2	+0.4

TABLE III. Reduction of Working Loss

Formula	Processing
6.0% Modified glycol acetal	Padded at 65% wet pick-up
2.5% Magnesium chloride catalyst	Frame dried (cure oven in tandem)
2.0% Fatty softener	Cured 90 sec. at 300° F.
0.1% Wetting agent	Sanforizer compressed

Evaluation		
Greige yardage on lot selected		5003
Yardage after preparation for treatment		5281
Guaranteed return on lot		4753 (95%)
Average return		4775 (95.3%)
Actual return this lot (less seams and samples)		4917 (98.3%)
Gain in yield		3.0%
Tensile strength, lb.	Prepared	123 × 67
	Finished	102 × 72
	Loss	15%
Warp shrinkage, %	Prepared (this lot)	9.1
	Finished (this lot)	0.9
	General average	1.0–1.5
Chlorine retention (this lot)		0

efficiency factor which describes the gain in crease resistance in relation to the major loss of tensile strength: efficiency factor = CRI/MTL.

CRI is the crease resistance increase; i.e., the crease resistance of the finished fabric minus the crease resistance of the fabric before finishing. Thus, a fabric having a 175° (W + F) crease resistance before finishing and a 250° crease resistance after finishing has a CRI of 75°. MTL is the major percentage tensile loss, whether warp or filling.

If the same fabric loses 37½% tensile strength in the filling and less than that in the warp, the efficiency factor of that treatment is 75/37.5 or 2.0.

Examination of the data from numerous treatments, both in the laboratory and in the mills, indicated for mill treatments that an efficiency factor of 2.0 is fair and one of 2.5 is good. The values for laboratory treatments are generally somewhat higher than those for mill finishing work.

Laboratory Investigation of the Properties of the Improved Glycol Acetal

Laboratory evaluations were carried out in order to determine the best conditions for the application of this new glycol acetal reactant. Cotton sheeting (80 × 80) was used for this work.

Figure 1 indicates the general range of crease resistances which may be obtained from the use of this new product. Higher applications will yield still higher crease resistances, but are also less practical from the point of view of cost. Under conditions of very firm curing, crease resistances up to 290° (warp plus filling) were obtained, but as might have been expected of such high crease resistance, the accompanying tensile losses went above 40%. Figure 2 depicts the corresponding range of tensile loss to be expected from the concentrations of reactant employed. Tensile reductions by this newer and more complex glycol acetal are of the same

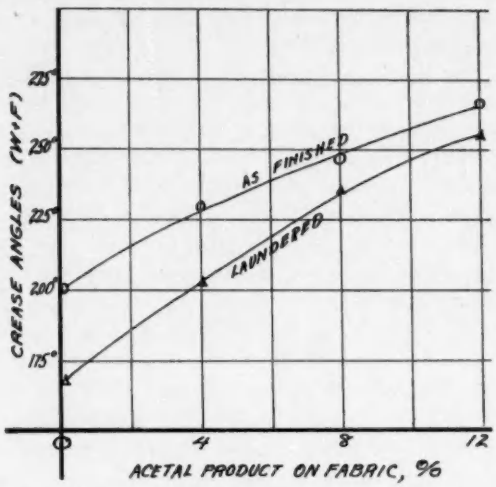

Fig. 1.

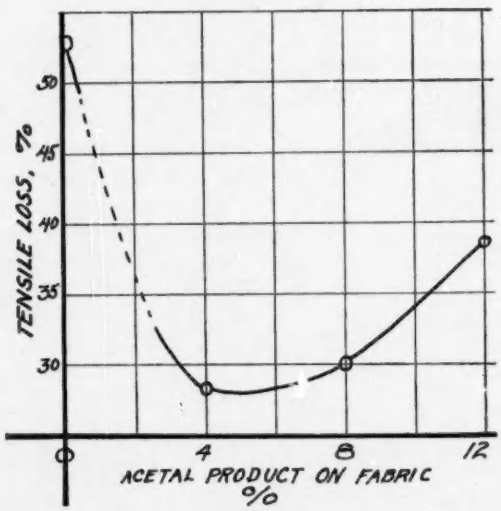

Fig. 2.

order as those for most of the commercially available thermosetting resins which impart similarly good crease resistances. The high tensile loss at zero acetal reactant is caused by the effect of catalyst alone.

Although Figure 1 indicated a continuing rise in crease resistance with increasing concentration of reactant and Figure 2 displayed an increasing tensile loss with increasing concentration of reactant, a plot of the efficiency factor against concentration (Figure 3) indicates that 8% of the product on the weight of the fabric will probably be the most satisfactory application because it will yield the highest crease resistance increase per percent of the major tensile loss.

Magnesium chloride was found to be the most satisfactory of the currently used catalysts. Figure 4 indicates a steady rise in crease resistance over a wide range of catalyst concentrations. Figure 5 shows a corresponding rise in tensile loss over the same range of magnesium chloride catalyst concentrations. A plot of the efficiency factor (Figure 6),

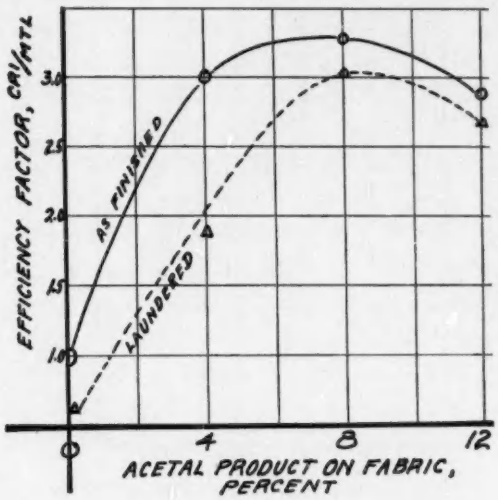

Fig. 3.

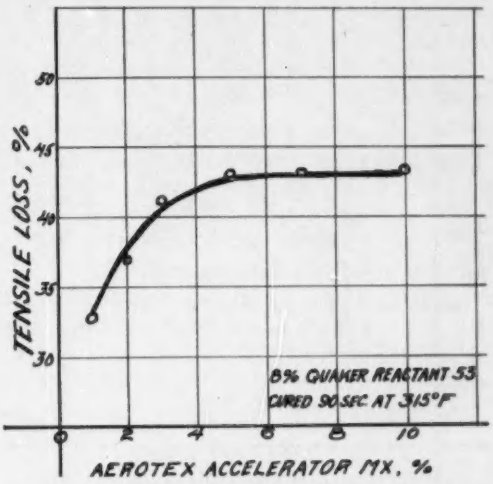

Fig. 5. Cured 90 sec. at 315° F.; 8% reactant 53.

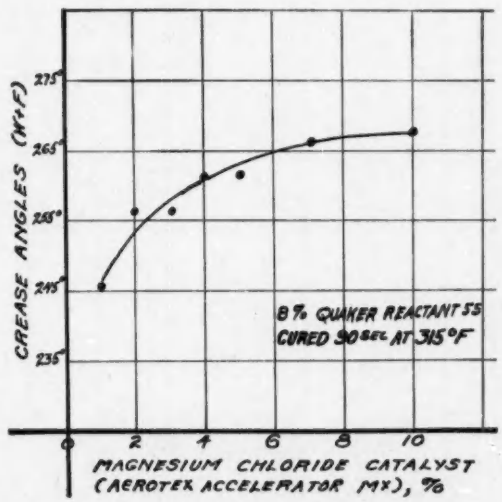

Fig. 4. Cured 90 sec. at 315° F.; 8% reactant 53.

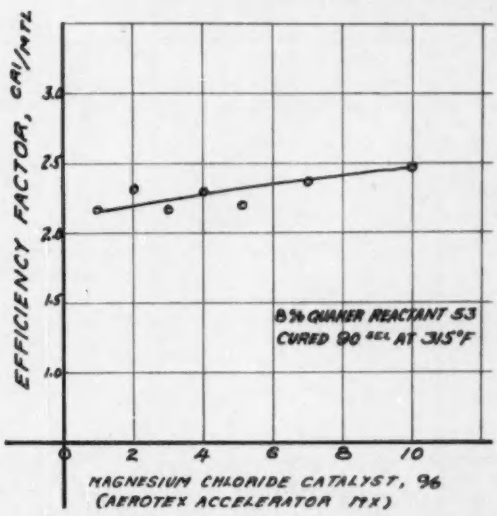

Fig. 6. Cured 90 sec. at 315° F.; 8% reactant 53.

however, indicates that, as far as concentration of the catalyst is concerned, there is no optimum quantity.

By use of a concentration of 4% Aerotex Accelerator MX a range of time and temperature combinations was examined (Figure 7); obviously the crease resistance rises sharply as the temperature of curing is increased. Figure 8 shows that the major tensile loss also rises with increasing curing temperatures. A plot of the efficiency factor vs. cure temperatures (Figure 9) clearly indicates the best curing temperature to be near 310° F. for curing times of 60–90 sec. This has since been confirmed repeatedly in production work.

The time required for cotton fabrics to pass through most mill curing ovens varies from 30 sec. to 2 min. Figure 10 indicates that curing at 290° F. within these time limits is probably too low to give acceptably high crease resistance. In Figure 11 it can be seen that 330° and 350° F. are curing temperatures which may cause drastic tensile loss unless the time is controlled within narrow limits. Plots

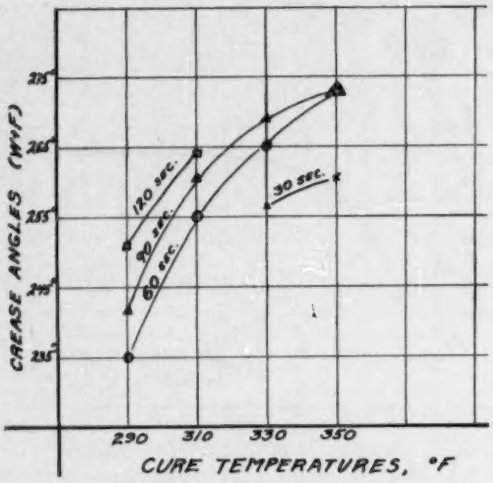

Fig. 7. Reactant 53 (8%).

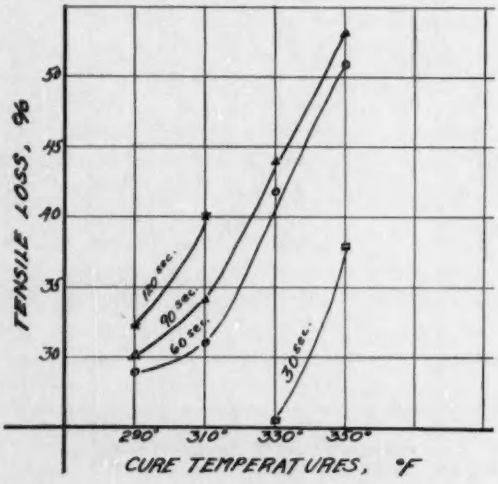

Fig. 8. Reactant 53 (8%).

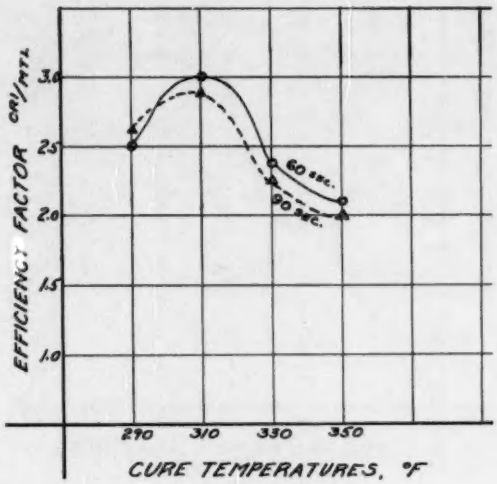

Fig. 9. Reactant 53 (8%).

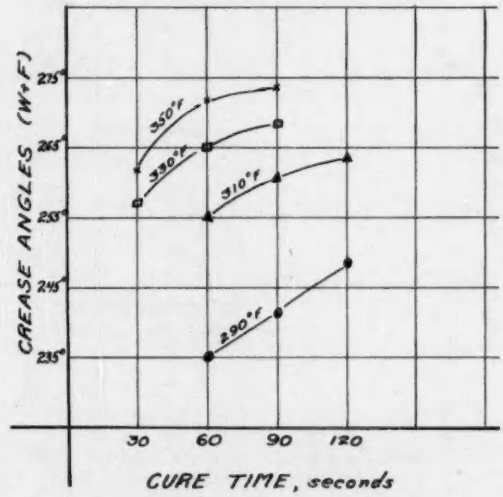

Fig. 10. Reactant 53 (8%).

of the efficiency factors vs. curing times at four temperatures (Figure 12) indicate 310° F. to be the most satisfactory curing temperature and 60–90 sec. to be the best curing times.

This highly crease-resistant modified glycol acetal has been commercially available for only a few months. During that period of time, the properties of high crease resistance, chlorine safety, and freedom from the possibility of odor development have led the product into steadily growing commercial use, particularly on white goods.

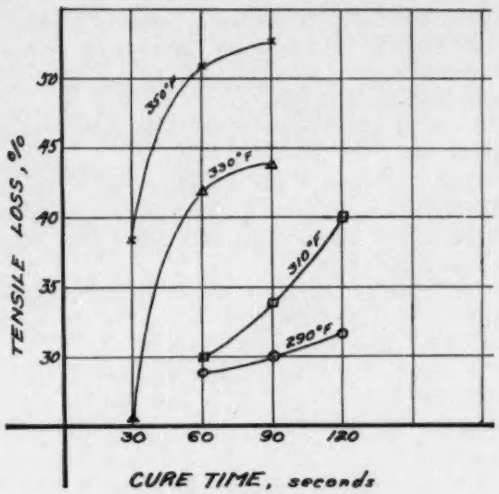

Fig. 11. Reactant 53 (8%).

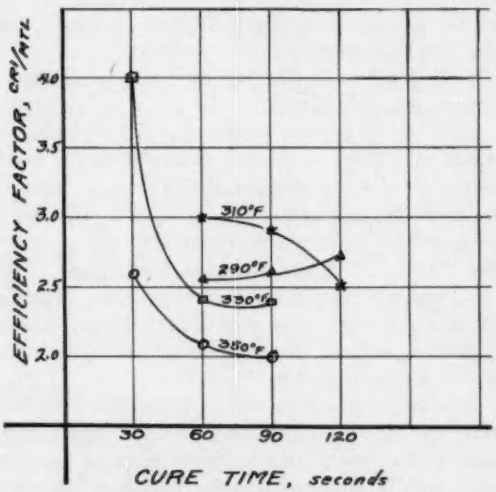

Fig. 12. Reactant 53 (8%).

The chlorine safety of the product is also of interest for goods printed on white background and for yarn-dyed fabrics which contain a preponderancy of white. This does not mean that the product has been limited to white goods and white background prints, for it has certainly found use on several types of dyed fabrics.

Textile Mill Applications and Evaluations of the Improved Glycol Acetal

Textile mill experiences with the new acetal reactant have borne out the findings of the laboratory investigations with regard to ease of curing and the other properties previously mentioned.

Easy care sheeting fabrics have been the subject of several recent announcements and of considerable mill finish development work. Chlorine safety, high crease resistance, and wash durability are the properties which make this new acetal reactant effective for the finishing of easy care sheeting.

Table IV presents the evaluation data for a mill finishing treatment carried out for the purpose of producing an easy care percale sheeting.

Ten percent reactant at 65% wet pickup is somewhat more than the optimum quantity of 8% pre-

TABLE IV. Percale Sheeting

Formula	Processing
10.0% Acetal reactant	Padded at 65% wet pick-up
6.0% Magnesium chloride catalyst	Predry and frame dry
	Cure 80 sec. at 320° F.
4.0% Polyethylene softener	Top soften and dry
0.2% Wetting agent	Calender
Bluing and optical white	

		Evaluation		
		Untreated	Acetal treated	Triazine treated
Tensile strength, lb.		67 × 71	47 × 46	43 × 40
Major tensile loss, % (MTL)			35	44
Crease angles	original	157°	249°	255°
	increase (CRI)		92°	98°
	after 5 washes		242°	244°
CRI/MTL			2.6	2.2
Tear strength, lb.		2.2 × 2.2	2.2 × 2.1	1.9 × 1.8
Chlorine damage		4%	0	0
Wash-wear rating	original		5	5
	5 washes		4	4

viously indicated. The high concentration of polyethylene softener was used to preserve tear strength.

The curing conditions employed here may at first glance appear to have been more vigorous than dictated by laboratory investigation, but in this case the fabric entered the cure oven cold so, if anything, the cure is probably mild instead of firm.

TABLE V. Muslin Sheeting, 64 × 64

Formula	Processing
15.0% Acetal reactant 5.0% Magnesium chloride catalyst 2.0% Polyethylene softener 0.6% Polyvinylacetate emulsion 0.1% Wetting agent	Padded at 60% wet pick-up Frame dried at 350° F. } in Cured 80 sec. at 320° F. } tandem Afterwashed and top softened Sanforizer compressed

Evaluation: After 10 1-hr. launderings at 212° F.

	Untreated	Treated
Tensile strength, lb.	65 × 69	42 × 36
Major tensile loss (MTL), %		48
Crease angles	171° initial—170°	246° initial—279°
CRI		109°
Chlorine damage, %	7	0
Wash-wear rating		4+
CRI/MTL		2.3

TABLE VI. Muslin Sheeting

Formula	Processing
12.0% Acetal reactant 4.5% Magnesium chloride hexahydrate 2.0% Nonionic fatty softener 0.1% Wetting agent	Padded at 70% wet pick-up Can dried Cured 70 sec. at 310–320° F. Afterwashed and top softened Calendered

Evaluation

	Untreated	Treated
Tensile strength, lb.	74 × 65	44 × 43
MTL, %		41
Tear strength, lb. (Elmendorf)	1.6 × 1.3	1.4 × 1.1
CRI		69°
Crease angles { original	171°	240°
Crease angles { 5 washes		230°
Chlorine damage, % { 1 wash	1	0
Chlorine damage, % { 5 washes	6	0
Wash-wear rating	1	5−
	2−	5−
CRI/MTL		1.7

The filling tensile loss of 35% coupled with a 92° increase in crease resistance gave an efficiency factor of 2.6 for this particular treatment.

The crease resistance exhibited excellent wash durability.

It can be seen that the tear strength of the fabric was successfully protected by the polyethylene softener. Complete chlorine safety was obtained.

Fabrics were wash-wear rated after tumble drying and under these circumstances were quite good; however, it would have been necessary to treat in a slightly more vigorous manner to obtain equally good hang-dried ratings.

Excellent whites were obtained on this sheeting fabric.

Table V presents the evaluation of a muslin sheeting which was given a very hard cure to obtain crease angles which would stay above 240° after several launderings.

The frame and cure box are set up in tandem at this mill; therefore the fabric enters the cure oven hot. This fabric was cured 80 sec. at 320° F.

The evaluation of this muslin was made after 10 Sanforizer wash tests; it can be seen that the crease resistance did indeed stay above 240° (W + F) as desired.

The use of slightly more than the optimum amount of acetal reactant coupled with a firm cure made this possible, but note that it was at the expense of 48% tensile loss in one direction, thus producing an efficiency factor of 2.3.

Hang-dried wash-wear rating after the ten launderings was satisfactory.

In Table VI another muslin sheeting treatment is evaluated. There were two objectives in the treatment of this fabric; retention of filling tensile strength above 40 lb. and reasonably acceptable wash-wear rating. The 240° crease resistance washed down only 10° in 5 high-temperature launderings. The fabric was completely resistant to chlorine degradation. Wash-wear ratings at 5 and 10 launderings were 5 −, and an efficiency factor of 1.7 was obtained on this treatment.

This sheeting fabric demonstrates the fact that there are circumstances where finish requirements make it desirable to dry and cure fabric less vigorously than is recommended for optimum efficiency. The previous fabric (Table V) is an example of

finish requirements which make it necessary to dry and cure more drastically than recommended. In such cases maximum treating efficiency (CRI/MTL) is not obtained.

A white cotton 124 × 56 sateen was processed for the purpose of obtaining crease resistances which would remain above 240° after several severe launderings. The data presented in Table VII are those obtained after 10 1-hr. launderings at 212° F. The crease resistance at 248° (W + F) after severe laundering was quite satisfactory, considering the fact that the processing formula contained a polyvinyl acetate emulsion. These latter materials usually detract from the initial crease resistance of finished fabrics. The initial presence and gradual wash removal of that polyvinyl acetate emulsion may be the reason that the fabric was wash-wear rated only 4 + originally and went up to 5 − after the series of launderings.

The rapidly spreading use of wash-wear garments has prompted considerable searching for permanently stiff, chlorine-safe white interlining fabrics. The fabric treated and tested as indicated in Table VIII appeared to have suffered practically no tensile loss. This was, however, probably caused by the gluing action of the large quantity of stiffening agent. The fabric exhibited a good, springy resilience and maintained its stiffness and interlining qualities throughout the 10 washes of the testing period. Wash-wear ratings of 5 originally and 4 after the series of launderings are surprisingly good in a fabric as stiff as this. A comparison of the wash durability with that of the fabric stiffened without the addition of the

TABLE VII. Sateen, 1.75 yd./lb.

Formula	Processing
15.0% Acetal reactant	Padded at 60% wet pick-up
5.0% Magnesium chloride catalyst	Frame dried
2.0% Polyethylene softener	Cured 80 sec. at 330° F.
1.6% Polyvinyl acetate emulsion	Afterwashed and top softened
0.1% Wetting agent	Sanforizer compressed

Evaluation	Untreated	Treated
Tensile strength, lb.	140 × 76	85 × 46
MTL		39½%
Crease angles (wt + f) original	177°	275°
Crease angles (wt + f) 10 washes		248°
CRI		98°
CRI/MTL		2.5
Chlorine damage, % (10 washes)	6	3
Wash-wear rating original		4+
Wash-wear rating 10 washes		5−

TABLE VIII. Interliner Fabric

Formula	Processing
18.0% Acetal reactant	Padded at 70% wet pick-up
5.0% Magnesium chloride hexahydrate	Dried on swing tenter
7.0% Polyvinyl alcohol	Cured 180 sec. at 305° F.
0.3% Wetting agent	Afterwashed
+Bluing and optical white	Dried on tenter frame

Evaluation	Untreated	Polyvinyl alcohol only	Treated
Tensile strength, lb.	39 × 40		48 × 36
Stiffness (original)	2 × 1	35 × 16	19 × 14
Handlometer with 1-in. strips, 1 wash, 160° F.	1 × 1	10 × 4½	15 × 15
Handlometer with 1-in. strips, 10 washes, 160° F.	2 × 1		13 × 13
Chlorine damage, % original	0		0
Chlorine damage, % 10 washes, 160° F.	5		5
Wash-wear rating original			5
Wash-wear rating 5 washes			4

TABLE IX. 1.48 Twill

Formula	Processing
12.0% Acetal reactant	Padded at 70% wet pick-up
4.0% Magnesium chloride hexahydrate	Predried on cans and frame dried
2.0% Polyethylene softener	Cured 2 min. at 320° F.
0.1% Wetting agent	Afterwashed and dried
	Sanforizer compressed

Evaluation	Untreated	Treated
Tensile strength, lb.	210 × 84	113 × 46
MTL		46%
Crease angles (w + f)	146°	260°
CRI		114°
CRI/MTL		2.5°
Chlorine damage, % original	5	0
Chlorine damage, % 10 washes	5	8
Wash-wear rating original	3	5
Wash-wear rating 5 washes	3	5

TABLE X. 7.2-Oz. Duck

Formula	Processing
12.0% Acetal reactant	Padded at 75% wet pick-up
4.0% Magnesium chloride hexahydrate	Frame dried-batched hot on roll
	Cured 2 min. at 320° F.
2.0% Polyethylene softener	Afterwashed and dried
0.1% Wetting agent	Sanforizer compressed

Evaluation	Untreated	Acetal treated	DMEU treated
Tensile strength, lb.	144 × 90	88 × 50	84 × 48
MTL		44%	46%
Crease angles	156°	257°	262°
CRI		101°	106°
CRI/MTL		2.3	2.3
Chlorine damage, % original	10	8	4
Chlorine damage, % 10 washes	3	5	75
Wash-wear rating original	3	5	5
Wash-wear rating 5 washes	3	5	5

TABLE XI. Oxford, 88 × 52

Formula	Processing
10.0% Acetal reactant	Padded at 65% wet pick-up
4.0% Magnesium chloride catalyst	Frame dried
	Cured 80 sec. at 315° F.
2.0% Polyethylene softener	Afterwashed and dried
0.1% Wetting agent	

Evaluation	Untreated (black and red)	Treated (black and red)	Treated (black and white)
Tensile strength, lb.	61 × 53	39 × 32	38 × 33
MTL		40%	38%
CRI		84°	84°
Crease angles original	178°	262°	262°
Crease angles 10 washes		258°	254°
Chlorine damage, % 1 wash	36	21	12
AATCC 69–52 10 washes	55	16	8
Chlorine damage (10 washes, Tide and Clorox), %	36	13	0
Wash-wear rating	1–2	4 +	4 +
	2	5 −	5 −
CRI/MTL		2.1	2.2

acetal reactant demonstrated the stiffness durability imparted by the latter. The acetal-treated fabric was completely chlorine-safe.

Table IX presents the evaluation of a 1.48-yd. twill which was finished to obtain a wash-fast wash-wear effect.

The major tensile loss of 46% produced by this firm cure was accompanied by a crease angle increase of 114° to give an efficiency factor of 2.5.

Even though this twill was dyed, the producer considered that chlorine safety was important because such fabrics "frequently are freshened with Clorox." The fabric was chlorine safe as finished and after 10 launderings at 212° F.

Tumble-dried wash-wear ratings of 5 before and after the series of launderings are what should be expected of a twill fabric with a crease angle total of 260°.

Table X illustrates an application of the acetal reactant to obtain wash-wear effects on a printed fabric with a white background.

In this case the acetal finish was compared directly to a dimethylol ethylene urea treatment for wash-wear effect, both originally and after five launderings. This duck fabric lends itself very well to wash-wear finishing, and both products rated 5 before and after the laundering series.

Chlorine retention was of importance on this fabric because it had a background of white. It is evident that fabric treated with the acetal reactant was chlorine safe even after the series of launderings, whereas that treated with the DMEU displayed increasingly severe chlorine damage.

A reasonably good crease resistance was obtained on the fabric, and the efficiency factor of the treatment was 2.3.

Yarn-dyed oxford fabrics, one in white and black and one in two colors, were treated for wash-wear effects. Chlorine safety was an important objective on the white and black fabric, but was of only academic interest on the two-color oxford. However, the untreated cloth used for testing comparison was from the two-color lot. The fabrics were of the same construction.

It is interesting to observe (Table XI) that the acetal reactant treatment reduces the chlorine damage potential caused by the presence of the dyes. This has been observed on several occasions where it has been necessary to run chlorine damage tests on partly dyed fabrics. Chlorine damage on the black and white fabric was low initially and was below 10% after 10 launderings.

In this case the fabrics were also subjected to a series of regular home launderings, with Tide and Clorox used in each laundering sequence. Under those conditions also, the chlorine safety on the black and white fabric is obvious; on the two-color fabrics the same protection of the dyes by the acetal can be noted.

The high wash-durable crease resistances were in keeping with wash-wear ratings, which were slightly better after five launderings than initially.

Table XII presents another fabric with mixed white and dyed yarns.

A 4 yd./lb. yarn-dyed shirting was processed with a chlorine-safe wash-wear effect in mind.

The shirting is a more difficult fabric upon which to get a good wash-wear rating, especially when compared with the oxford. The initial crease angle total of 265° gave the shirting wash-wear ratings of 4. The oxford just discussed had slightly lower crease angles, but somewhat higher wash-wear ratings. The important contribution of fabric construction to this difference can be seen in the wash-wear ratings of the untreated fabrics. That of the oxford was 2 and that of the shirting is 1.

There are many finishing formulas where the concentrations of finishing resins and catalysts must be kept low to preserve the tensile strength of the fabric. Such a case is presented in Table XIII, where an application of only 5.4% of the modified glycol acetal was used to produce crease-resistant finishes. In this case, one fabric was direct dyed and the other was vat dyed. The acetal protection against chlorine degradation due to the presence of dye is again obvious. This evaluation table demonstrates that a quantity of acetal reactant below that considered optimum may be used to produce a satisfactory effect. The crease resistances before and after laundering demonstrate the excellent durability which may be obtained by the use of acetal reactants.

An interesting distinction between the new modified glycol acetal and a dimethylol ethylene urea has been observed in the treatment of a Cibacron dyed fabric. A fabric processed with the dimethylol ethylene urea showed very poor lightfastness, having faded noticeably after 10 hr. An untreated blank and a fabric processed with the acetal reactants displayed equally good lightfastness through the first 20 hr. and a barely perceptible fading at 40 hr. This preliminary lightfastness investigation on the cellulose reactant type dyes is not intended to indicate that the acetal reactant finish will protect all such dyes. Certainly, however, there is some indication that it may be a useful product for treatment of Cibacron dyed fabrics.

TABLE XII. Shirting

Formula	Processing
12.0% Acetal reactant	Padded at 60% wet pick-up
4.0% Magnesium chloride catalyst	Frame dried / Cured 70 sec. at 325° F. (in tandem)
2.0% Polyethylene softener	Afterwashed
1.0% Starch ether	Frame dried
0.1% Wetting agent	

Evaluation	Untreated	Treated
Tensile strength, lb.	62 × 44	45 × 27
Crease angles (original)	185°	265°
Crease angles (10 washes)		253°
Chlorine damage, % (1 wash)	14	21
Chlorine damage, % (10 washes)	18	12
Chlorine damage after 10 washes with Tide and Clorox, %	5	8
Wash-wear rating (original)	1	4
Wash-wear rating (5 washes)	1	4

TABLE XIII. Gingham, 96 × 60

Formula	Processing
7.2% Acetal reactant	Padded at 75% wet pick-up
3.8% Magnesium chloride hexahydrate	Frame dried to 5% moisture
0.8% Polyvinyl alcohol	Cured 2 min. at 310° F.
0.7% Cationic softener	Afterwashed and frame dried
0.1% Wetting agent	

Evaluation	Direct dyed		Vat dyed	
	Untreated	Treated	Untreated	Treated
Tensile strength, lb.	67 × 35	52 × 25	47 × 28	35 × 19
MTL		29%		32%
Crease angles (original)	178°	250°	174°	252°
Crease angles (5 washes)		246°		252°
CRI		72°		78°
CRI/MTL		2.5		2.4
Chlorine damage, % (1 wash)	30	8	12	5
Chlorine damage, % (5 washes)	47	15	15	9

Low Temperature Catalysts of the Improved Glycol Acetal

A different catalyst, the chemical nature of which has not yet been disclosed but which is currently available under the proprietary designation "Catalyst RCL," has been used to cure the new acetal reactant at lower temperatures and/or shorter times.

Figure 13 shows an original crease resistance range higher than that previously shown with the magnesium chloride catalyst at 315° F. With the magnesium chloride catalyst (Figure 4), the crease resistance ranged from 245° to about 270°, and here it can be seen that the range with this catalyst is from 255° to 285°. Figure 13 also shows a laundry loss of about 25–30° and indicates a very sharp loss of washfastness of crease resistance where curing was done below 250° F. Figure 14 indicates tensile losses to be of the same order as those obtained with magnesium chloride (see Figure 5). Plots of the efficiency factor, Figure 15, against the curing temperature for laundered and unlaundered pieces make it clear that at the time of 1 min. at 250° F. is the

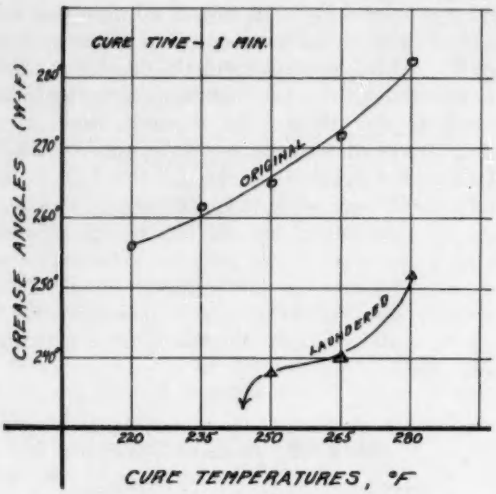

Fig. 13. Cure time 1 min.

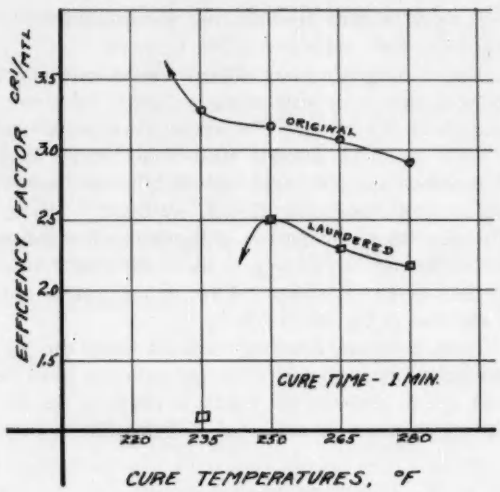

Fig. 15. Cure time 1 min.

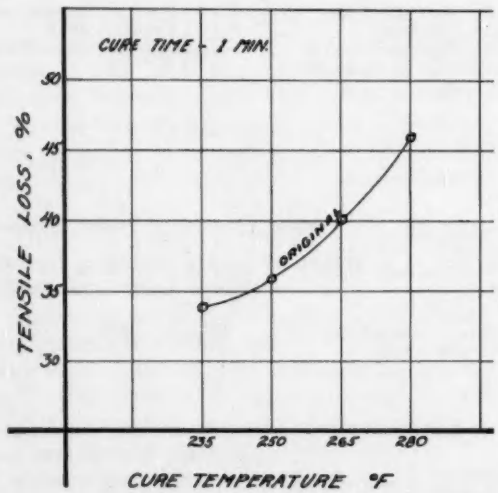

Fig. 14. Cure time 1 min.

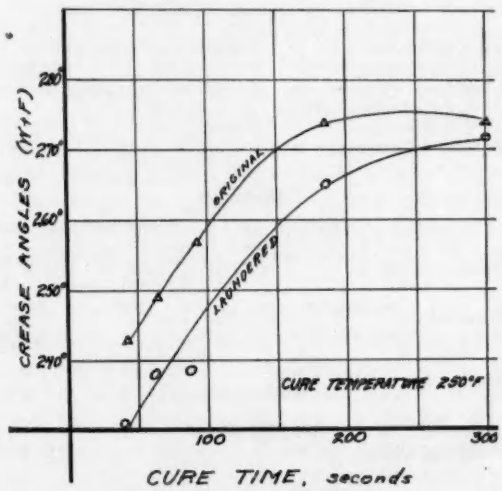

Fig. 16. Cure temp. 250° F.

minimum satisfactory cure temperature. Below 250° F. the crease resistance washes down so badly that it is obvious that the fabric is insufficiently cured.

A range of times from 45 sec. to 5 min. was studied at 250° F. curing. Figure 16 indicates that crease resistance increases up to about 180 sec. cure time. Beyond that time there is no additional crease resistance obtained. The curve for laundered crease resistance indicates that there is a very slight increase in durability between 180 sec. and 300 sec.

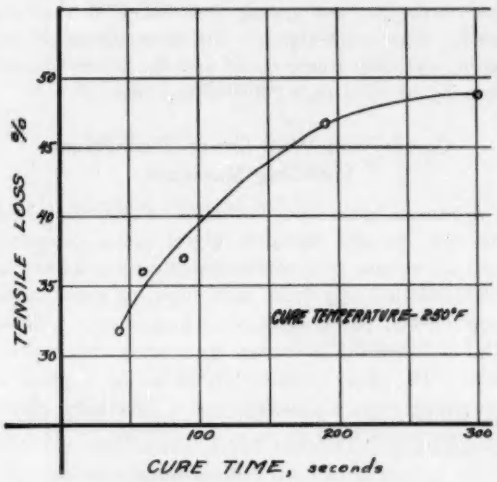

Fig. 17. Cure temp. 250° F.

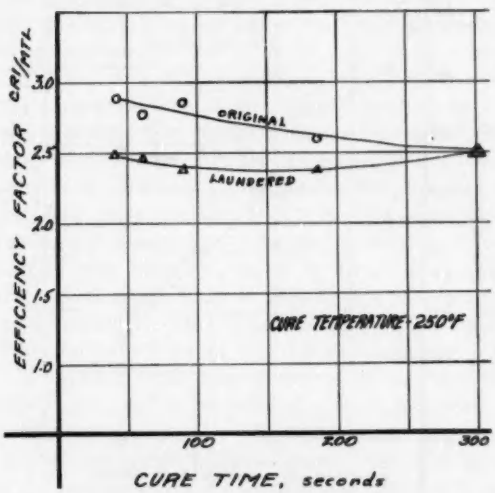

Fig. 18. Cure temp. 250° F.

Figure 17 shows that tensile loss rises from 33 to 49% over the period of time between 45 sec. and 5 min. In this case also, the time beyond 3 min. has practically no effect. This indicates much more safety with regard to time than is available from a normal catalyst system. With the magnesium chloride catalyst system, a cure temperature which would be satisfactory at 1½ min. would be destructive at 5 min. In Figure 18 the efficiency factor plot shows that there is no optimum time which gives a superior crease resistance gain per percent tensile loss. This catalyst does not yield unusually low tensile losses in conjunction with high crease resistance.

The use of this catalyst offers three possibilities for curing advantages to textile mills.

1. Frame curing to save an operation.
2. More complete curing in ovens of limited heat capacity.
3. Faster curing in standard equipment, especially where the drying frame and cure box are set up in tandem.

The practice of two of these possibilities is presented here.

Textile Mill Applications With Low Temperature Catalysis

Table XIV compares parallel runs with magnesium chloride and with the high-speed catalyst. The

TABLE XIV. Poplin, 108 × 50

	Untreated fabric	Normal catalyst and cure	High-speed catalyst and cure
Acetal reactant		15%	12%
Magnesium chloride hexahydrate		4%	—
Catalyst RCL		—	9%
Polyethylene softener		2%	2%
Fatty softener		3%	3%
Wetting agent		0.2%	0.2%
Cure temperature, ° F.		315	275
Cure time, sec.		100	60
Frame and cure box speed, yd./min.		90	150
Tensile strength, lb.	105 × 50	72 × 31	79 × 39
Tensile loss, %		31 × 38	25 × 22
Crease angles	170°	252°	231°
CRI		82°	61°
CRI/MTL		2.2	2.4
Chlorine damage, % original	4	0	0
Chlorine damage, % 5 washes	0	4	5

TABLE XV. Muslin Sheeting

Formula	Processing
11.6% Acetal reactant 9.2% Catalyst RCL 0.1% Polyvinyl acetate 2.9% Polyethylene softener 0.1% Wetting agent	Impregnated, then partly dried on cans Dried and cured in frame 20–25 sec. at 305–330° F. Afterwashed, top softened, dried Calendered

Evaluation		Competitive wash-wear sheet	Acetal treated
Tensile strength, lb.	original	44 × 35	47 × 31
	10 washes	39 × 35	44 × 30
Tear strength, lb. (Elmendorf)	original	2.1 × 1.4	2.3 × 1.3
	10 washes	2.0 × 1.4	2.3 × 1.3
Crease angles	original	257°	243°
	10 washes	246°	249°
Scorching after 10 washes containing Clorox		severe	none

processing formulas differed slightly in reactant concentration.

The curing conditions for the normal system were 100 sec. at 315° F. Such cure conditions permitted the frame and cure box to be operated at a speed of 90 yd./min.

For the high-speed catalyst the curing conditions were 60 sec. at only 275° F., and the frame and cure box ran at 150 yd./min. This permitted a considerably increased rate of output of fabric.

The high-speed catalyst yielded slightly higher tensile strengths and lower crease resistances. This indicated that the temperature of the cure box could be raised another 10° or 20° to obtain results parallel with those of the normal catalyst and cure system while still maintaining the 150 yd./min. running speed. This was confirmed in practice. In the data for tensile loss it may be observed that the percent loss of tensile strength is more nearly the same in warp and filling than it is under the slower and hotter normal curing system. In fact, the filling exhibited lower loss of tensile strength than the warp. This is unusual in the crease resistance treatment of cotton fabrics. It is also to be considered an advantage, because the filling is usually weaker than the warp.

This was not an isolated occurrence. It has since been observed more than once in the use of the high-speed catalyst. The same balance of losses has also occurred on the tear strengths of fabrics thus treated.

Efficiency factor for the high speed catalyst was 2.4; that for the normal catalyst was 2.2. Both fabrics were chlorine-safe before and after a series of launderings.

In the case given in Table XV, the high-speed catalyst was used to prepare easy care sheeting without the use of conventional dry and curing equipment. In evaluation of the fabric it was compared to a sheeting from another mill. The fabrics were of similar but not identical structure. The tensile strengths, tear strengths, and crease resistances of the two fabrics were approximately the same, although one fabric was only frame cured and the other was reportedly handled in a conventional manner.

Comparison With Other Wash-Wear Finishing Materials

A resumé evaluation was made to determine how the new complex modified glycol acetal compares with other types of products which are considered in the textile industry to be candidates for good wash-wear effects, particularly for white fabrics. Table XVI is based on laboratory treatments and evaluations. The new modified glycol acetal, a triazine containing resin, a triazone, and a dimethylol ethylene urea were used to make comparable treatments

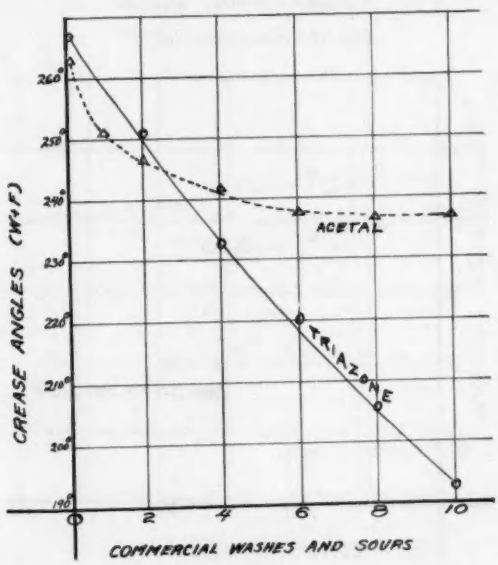

Fig. 19.

TABLE XVI. White Fabric Wash-Wear Finishing Agents
Laboratory Comparison of General Properties

	Acetal reactant	Triazine-containing resin	Triazone	DMEU	Blank
Crease angles { original	263°	278°	275°	277°	158°
Crease angles { 10 washes	240°	258°	251°	257°	157°
CRI	105°	120°	117°	119°	—
Wash-wear ranking { 1 wash	3rd	4th	2nd	1st	5th
Wash-wear ranking { 30 washes	2nd	4th	1st	3rd	5th
Tensile loss, % (MTL)	41	47	37	44	—
CRI/MTL	2.6	2.6	3.2	2.7	—
Accelerator abrasion loss, %	6.2	12.3	10.6	8.7	1.6
Chlorine damage, % AATCC 69–52 { 1 wash	2.5	1	2.5	5	2
Chlorine damage, % AATCC 69–52 { 5 washes, 212° F.	0	0	4	60	7
Chlorine damage, % AATCC 69–52 { 30 washes, 160° F.	3	0	0	>75	19
Scorching, 60 sec. at 365° F.	← All satisfactory →				
Scorching rank, 30 sec. at 420° F.	3	2	5	4	1
Tensile strength, household Clorox washes { 5W	26	26	29	27	50
Tensile strength, household Clorox washes { 5W ironed	25	27	26	15	50
Tensile strength, household Clorox washes { 20W	27	23	22	26	40
Tensile strength, household Clorox washes { 20W ironed	23	24	21	10	40

on 80 × 80 cotton sheeting. All four products are commercially available and considered to be among the leading candidates for the production of wash-wear finishes. In initial crease resistances the other three products were slightly higher than the modified glycol acetal. After 10 washes they have all washed down between 20° and 25°.

The acetal reactant yielded equivalent wash-wear ratings at crease resistances lower than those necessary for the other products to do the same. All wash-wear ratings with the exception of the blank were between 4 and 5. Because of the closeness of the wash-wear ratings, the finished fabrics were ranked for comparison. At the 1-wash level, the DMEU was best. However, at the 30-wash level, the relative appearances of these fabrics had changed somewhat. The DMEU had dropped to third place below both the triazone and the acetal reactant.

From the tensile loss figures it appears that the whole series of fabrics received a fairly firm cure.

With the exception of the triazone, the fabrics all display the same efficiency factor. Abrasion losses were determined by the Accelerotor method; it appears from the weight loss test that the two reactant type finishing agents (acetal and DMEU) may have a less severe effect on the abrasion resistance of the fabric than do the other two materials. Scorching of the fabrics was first tried at 360° F. for a period of 60 sec. All fabrics withstood this scorching test. Another scorching test employing temperatures of 420° at 30 sec. was applied to the fabrics and, under the conditions of that test, only the triazone produced an unacceptable appearing fabric. The AATCC chlorine damage test at 1, 5, and 30 launderings at the temperatures indicated shows that the acetal reactant, the triazone, and the triazine containing material are all chlorine-safe finishing agents.

An additional comparison was made between the acetal reactant and the triazone (Figure 19). In a commercial laundering operation in which zinc silico fluoride was used as a souring material, the modified glycol acetal washes down in crease resistance to about the same point that it does in other types of laundering; however, the crease resistance obtained from the triazone finish drops steadily and is almost completely eliminated at the end of ten such launderings.

Conclusion

Obviously no single one of the above four leading candidates for wash-wear finishes can supply the answer to all finishing problems. Each has its advantages and its disadvantages. It is believed that this new glycol acetal which imparts high, very durable crease resistance and does not suffer from the chlorine susceptibility problems of the DMEU or the amine odor development problems of the methyl and ethyl triazones will continue to expand its usefulness in the better quality wash-wear finishing of cotton.

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Chlorine Retention in Resin-Treated Cottons[1]

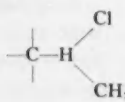
Hugh H. Mosher

Arkansas Company, Inc., Newark 1, New Jersey

COTTON fabrics react with certain methylol compounds under favorable conditions to acquire crush and shrink resistance properties. These characteristics render cotton goods less inclined to wrinkle and muss in use and simplify laundering and pressing operations, particularly the latter.

The methylol compounds most generally used to finish cottons are urea- and melamine-formaldehyde condensates and their derivatives. Changes in the internal structure of the cellulosic fibers are produced by these condensates. The exact nature of the change has not been determined. Stronger cross-linkages or bridges between the cellulose molecules which constitute the interior structure of cellulose fibers undoubtedly occur, and other alterations of the intrafiber structure are produced.

These changes in fiber structure are accomplished with a simultaneous development of certain adverse characteristics. A loss of tensile and tear strength occurs, and the cotton fiber acquires an ability to pick up chlorine from a hypochlorite bleach bath and form chloroamides.

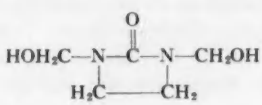


The chloroamides are unstable chemical compounds which may decompose at the temperature of ironing with a liberation of traces of hydrochloric acid. It is the release of this acid during ironing that impairs the strength of a bleached wash-and-wear fabric.

A considerable difference exists in the thermal stability of the chloroamides produced from the various wash-and-wear finishes. The chloroamides of dimethylol ureas and their methyl ethers are particularly unstable and are not recommended for application to "whites" or materials likely to be bleached. The chloroamides produced from melamine-formaldehyde condensates are more thermally stable than their urea prototypes. They do, however, yellow white goods, and melamine resins are not generally regarded as suitable for finishing cotton textiles which are subject to multiple launderings and bleachings.

The development of wash-and-wear cotton goods which will retain their crush and shrink resistance properties and be relatively free from damaging chlorine retention during their normal life expectancy, at least under home laundering conditions, resulted from the development of the so-called cyclic urea-formaldehyde condensates. The "cyclic ureas" at present constitute a restricted family of finishes;

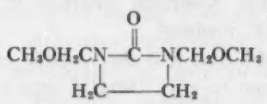
I



[1] Presented at the Chemical Finishing Conference of the National Cotton Council, Washington, D. C., October 1, 1958.

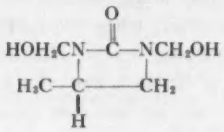
1,3 bis(hydroxymethyl)-2 imidazolidone
commonly known as dimethyol
ethylene urea (DMEU)

II



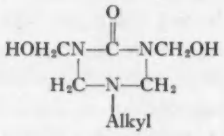
Dimethyl ether of DMEU

III



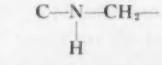
1,3 bis(hydroxymethyl) 5 methyl-2 imidazolidone

IV



1,3 dimethylol 5 alkyl perhydrotriazone
commonly known as Triazone

the most common are given above. The conventional urea- and melamine-formaldehyde condensates owe their adverse chlorine retentive properties to the presence of an amide radical:

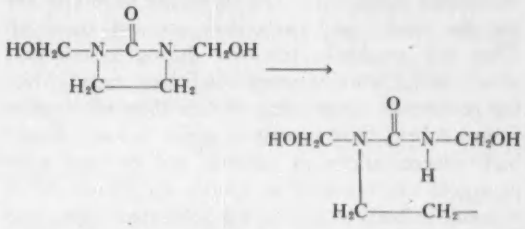


It is this radical which reacts with chlorine to produce the thermally unstable chloroamides. The nitrogen in the cyclic urea-formaldehyde compounds is theoretically completely blocked; no valences exist for entrance of chlorine atoms and, accordingly, cyclic urea-formaldehyde finishes should be chlorine resistant. This statement is more theoretical than real. A certain amount of unblocking occurs in the fixation of "cyclic urea" finishes onto cotton goods, with the result that the fabrics absorb a small amount of chlorine from a hypochlorite bleach bath.

Although cyclic urea-formaldehyde condensates are relatively stable chemical compounds which are not perceptibly altered in aqueous solutions by ordinary hydrolytic procedures, a similar stability is not secured when these compounds are affixed onto cotton fabrics. A small but variable amount of such finish, depending on the "tightness" of its set and other factors, is susceptible to hydrolysis to produce compounds which are potentially chlorine retentive.

The hydrolysis may be stimulated and occur during almost any operation to which the finished cotton goods may be normally subjected—laundering, bleaching, steaming, sunlight, or simple storage under adverse conditions.

The cause of the degradation of the finish has not been definitely established, but is believed due to some break in the cyclic urea ring with formation of a reactive amide radical:



It should not be concluded from the above that cyclic urea-formaldehyde finishes are easily degraded; quite the reverse is true. They rate among our most durable finishing agents. Only a small portion of the condensate is involved in hydrolytic procedures, and even this may be circumvented or minimized by a "tighter resin set" and suitable post-cure rinses.

Relation of Finishing Application to Chlorine Retention

Cyclic urea-formaldehyde condensates are generally affixed onto cotton goods by acid catalysts at elevated temperatures. It is highly desirable to set the finish in its most stable form with a minimal development of hydrolyzable impurities.

Although many types of acid catalysts have been proposed to set cyclics, those in most common use are the amine hydrochlorides, magnesium chloride, and zinc nitrate.

The amine hydrochlorides, in contrast to the magnesium and zinc salts, are stable in the presence of most softening agents and co-finishes such as water repellents, and are generally used when such auxiliaries are used with DMEU. Magnesium chloride, on the other hand, is less drastic in its action on cotton fabrics and catalyzes "resins" to produce wash-and-wear fabrics with slightly higher tensile and tear strength, whereas zinc nitrate produces a "tighter" and more durable resin set than any wash-and-wear catalyst in common use.

The finish of fabrics which have been set with metallic catalysts—magnesium chloride or zinc nitrate—is initially more resistant to acquiring damaging chlorine retention from a hypochlorite bleach

bath. This is due to an intrafiber deposition of metallic oxides and carbonates formed from the catalyst during curing. These tend to buffer cotton goods against acid damage, and they initially act as a sort of ion exchange resin, neutralizing any hydrochloric acid generated from retained chlorine during ironing and being regenerated during the subsequent laundering operation. The corrective effects of the metallic oxides and carbonates are but transient. They are gradually removed during laundering; slowly under home washing conditions, rapidly during commercial laundering. With their elimination from a fabric, their protective action is lost. Fairly high concentrations of catalyst and elevated temperatures are required to inhibit the formation of resinous radicals which, during subsequent aging and laundering operations, generate potentially damaging chlorine-retentive bodies.

Minimal chlorine-retentive wash-and-wear cotton goods are generally produced by setting the cyclic with the maximum concentration of catalyst and highest curing temperature that may be used without producing an excessive deterioration of the fabric.

The influence of the concentration of the acid catalyst and curing temperature on the potential chlorine retentivity of cotton goods finished with DMEU are shown in the accompanying tables.

Swatches of 80 × 80 scoured and bleached cotton goods containing approximately 5% DMEU which had been set with variable amounts of catalyst and at different curing temperatures were used for the tests. All of the samples were finished on a three-roll Butterworth 10-in. pad using a double dip, double nip threading with a roll gauge pressure of 40 lb., which produced a wet pickup of approximately 75%. The fabrics were then dried at 160° F., cured at a predetermined time and temperature, and rinsed, first in a 0.125% soda ash solution and finally in cold water until free from alkali. The swatches were dried after rinsing and aged in a conditioning room maintained at 70° F. and 65% relative humidity for one month. Subsequent to conditioning, the fabrics were divided in groups and exposed to different laundering conditions.

One set was exposed to the full cycle of automatic home laundry machine using 0.2% of Tide, an alkaline detergent preparation, and 0.01% of available chlorine, the concentration of bleach recommended for home use. The second set was laundered for 30 min. at 160° F. in a dilute soap solution (Lux), whereas the third set was laundered in accordance with the white laundering procedure recommended by the American Institute of Laundering for commercial washing.

This test indicates that the variable concentrations of catalyst used to affix DMEU onto cotton fabrics do not produce finishes which hydrolyze significantly under conventional home laundering and bleaching procedure. However, when the fabrics are exposed to a drastic bleaching action, like that indicated in the last column of Table I, the value of more catalyst to produce a firmer set becomes apparent.

The influence of higher concentrations of catalysts on DMEU during curing to inhibit the development of precursors having damaging chlorine retention during laundering is more apparent with cotton goods washed under more vigorous conditions.

The results summarized in Table II indicate the value of higher concentrations of catalyst in affixing DMEU during curing and in inhibiting the tendency of the finish to hydrolyze in subsequent laundering operations to produce a fabric easily damaged during bleaching and ironing.

Although cyclic urea-formaldehyde condensates when properly affixed onto cotton goods produce finishes with sufficient durability and chlorine resistance to withstand all ordinary home laundering and bleaching conditions, a hazard exists when such materials are exposed to commercial laundering.

DMEU finishes, even when set onto fabrics in their most stable form, hydrolyze at the high temperatures and strongly alkaline solutions used by commercial launderies, causing a loss of finish substance and the development of potential chlorine retentive properties.

Residues of acidic antichloro from the last step of the commercial laundering cycle are also present on the washed fabrics. The influence of this acidity is discussed later in this paper.

A number of cyclic urea-formaldehyde condensates exist, but only DMEU and the triazones are extensively used in finishing wash-and-wear cottons. The dimethyl ether of DMEU and its alkyl derivative 1,3 bis (hydroxy methyl) 5-methyl-2-imidazolidine produce finishes somewhat more chlorine resistant, but do not show sufficient improvement to justify their use from a price consideration. The triazones, which have a tertiary nitrogen radical in their structural configuration that functions some-

what like an ion exchange resin, are discussed in another paper at this conference.[2]

The temperature of curing is as important as the concentration of catalyst in producing a finish on cotton goods resistant to the development of damage due to chlorine retention during bleaching and ironing. The influence of the temperature factor is shown in Table IV. The results indicate that a firmer set of DMEU is secured on cotton goods at more elevated curing temperatures.

[2] Given by Rosser L. Wayland, Jr.; scheduled for publication in February.

Influence of Atmospheric Agencies on Cyclic Urea-Formaldehyde Resins

Cyclic urea-formaldehyde condensates, when affixed on cotton goods, may be sensitized to change

TABLE I. Effect of Variable Resin Fixation on Development of Damaging Chlorine Retention (Home Laundering)

Variables—catalytic concentration
Fabric—80 × 80 cotton goods
Laundering—automatic home laundering at 120° F.

Sample	Conc. of catalyst	Time and temperature of curing	Initial strength, warp	Strength after 1 wash	Strength after 10 washes	Strength after 20 washes	Strength after 20 washes + AATCC 69–1952
Water	0	3 min. at 310° F.	56	55	52	51	51
5% DMEU	⅛% Zinc nitrate	3 min. at 310° F.	40	38	37	32	9
5% DMEU	¼% Zinc nitrate	3 min. at 310° F.	38	39	37	35	18
5% DMEU	½% Zinc nitrate	3 min. at 310° F.	38	36	35	35	33
5% DMEU	¾% Zinc nitrate	3 min. at 310° F.	36	34	35	34	34

All tensile strength figures express in pounds; all samples ironed at cotton setting of iron after each wash.

TABLE II. Effect of Variable Resin Fixation on Development of Damaging Chlorine Retention (High Temperature Washing)

Variables—catalytic concentration during curing
Fabric—80 × 80 cotton goods
Laundering—½ hr. exposure to soap solution at 160° F. in automatic home wash

Sample	Conc. of catalyst	Time and temperature of cure	Initial strength, warp	Strength after 1 wash + AATCC 69–1952	Strength after 5 washes + AATCC 69–1952	Strength after 10 washes +.02% chlorine bleach	Strength after 10 washes + AATCC 69–1952
Water	0	3 min. at 310° F.	56	54	50	50	48
5% DMEU	⅛% Zinc nitrate	3 min. at 310° F.	40	9	—	10	5
5% DMEU	¼% Zinc nitrate	3 min. at 310° F.	38	16	—	27	8
5% DMEU	½% Zinc nitrate	3 min. at 310° F.	38	38	34	36	18
5% DMEU	¾% Zinc nitrate	3 min. at 310° F.	36	37	36	36	30

TABLE III. Damage Caused by Different Laundry Procedures

Variables—laundering procedures
Fabric—80 × 80 cotton goods

Sample	Catalyst	Laundering	Initial strength, warp	Strength after 1 wash (0.01% Cl)	Strength after 3 washes (0.01% Cl)	Strength after 3 washes + AATCC 69–1952
Water	0	Home method at 120° F.	56	54	53	55
5% DMEU	¾% Zinc nitrate	Home method at 120° F.	38	37	37	35
5% DMEU	¾% Zinc nitrate	Home method at 160° F.	38	37	38	35
5% DMEU	¾% Zinc nitrate	Commercial laundering	38	36	30	12

by factors other than washing. Storage of the finished fabric under improper conditions of pH, steaming, and possibly even sunlight modify the finish to give it potentially damaging chlorine retentive properties. Acidity is a major offender in accelerating this change. Even traces of acid have an adverse effect. The presence of these "progenitors of woe," as they have been called, are not apparent by a visual inspection of a fabric and often do not exhibit their effect until after the textile has been washed, bleached, and drastically ironed. The formation of damaging chlorine-retentive bodies from DMEU by traces of acidity is often exceedingly slow and does not become apparent until weeks, and in some cases months, have elapsed after a fabric has been processed. The importance of a neutral or slightly alkaline reaction on wash-and-wear fabrics to arrest the development of chlorine-retentive bodies during bleaching is not generally recognized by finishers.

It has been a rather common practice to simply mechanically finish resin-treated textiles after curing, leaving the catalyst un-neutralized in the cloth. Such materials not only tend to develop malodors during aging but are much more susceptible to damage during laundering and bleaching than fabrics prepared in accordance with recommended practices.

The influence of the pH of a cotton fabric finished with DMEU to acquire potentially damaging chlorine-retentive properties during storage is illustrated in tables below.

Table V illustrates the effect of omitting the final alkaline rinse with 130 × 60 cotton goods commercially finished with DMEU. All of the fabrics were finished so as to leave approximately 3.5% finish on the fabric. The finish was set with commercial

TABLE IV. Influence of Variable Temperature on Set of DMEU Finishes

Variables—temperature
Fabric—80 × 80 cotton goods

Sample	Conc. of catalyst	Curing condition		Initial strength, warp	Strength after 5 washes* + AATCC 69–1952	Strength after 10 washes* + AATCC 69–1952
		Min.	° F.			
Water	0	0		53	54	52
5% DMEU	⅛% Zinc nitrate	3	290	41	9	—
5% DMEU	⅛% Zinc nitrate	3	310	38	12	6
5% DMEU	⅛% Zinc nitrate	3	350	36	21	16
5% DMEU	½% Zinc nitrate	3	290	39	18	12
5% DMEU	½% Zinc nitrate	3	310	38	36	18
5% DMEU	½% Zinc nitrate	3	330	36	35	34
5% DMEU	½% Zinc nitrate	3	350	34	33	32

* All fabrics were washed in a dilute soap solution for 30 min. at 160° F.

TABLE V. Influence of Post-Cure Rinse on Development of Damaging Chlorine Retention

Fabric—130 × 60 cotton

Sample	Catalyst to set	Post-cure rinse	pH	Initial strength, warp	Strength after 1 wash + AATCC 69–1952	Strength after 3 washes + AATCC 69–1952
Water	—	—	—	96	94	94
3.5% DMEU	¾% Zinc nitrate	Alkaline	7.1	71	70	68
3.5% DMEU	¾% Zinc nitrate	—	5.2	70	46	21
3.5% DMEU	1% Magnesium chloride	Alkaline	7.2	76	72	70
3.5% DMEU	1% Magnesium chloride	—	5.8	73	39	18
3.5% DMEU	½% Amine hydrochloride	Alkaline	7.1	74	72	72
3.5% DMEU	½% Amine hydrochloride	—	5.7	76	21	16

These tests indicate that the presence of acid, as indicated by the pH of the water extract of the treated fabrics, sensitizes DMEU to degradation even during normal storage.

catalysts—zinc nitrate, magnesium chloride, or an amine hydrochloride—in a curing range for 3 min. at 310° F. Subsequent to curing, the fabrics were subdivided. Half of each piece was washed in a dilute soda ash solution, followed by a water rinse. The comparison half was mechanically finished without rinsing. The samples were aged for one month before testing. All wash tests on the aged fabrics were conducted in soap solutions for 30 min. at 160° F., to exaggerate the effects of home washing.

The influence of time and the pH of a cotton fabric finished with DMEU to produce damaging chlorine retention during storage are summarized in Tables VI, VII, and VIII. All of the samples were prepared on a laboratory pad so as to have 5% finish on the cloth, which was affixed with 0.75% zinc nitrate by curing for 3 min. at 310° F. Subsequent to curing, the swatches were washed, adjusted to a desired pH by chemicals, and tested for damaging chlorine retention after laundering by conven-

TABLE VI. Effect of Storage Time on Development of Damaging Chlorine Retention of Resin-Treated Cottons

Variables—pH and storage time
Fabric—80 × 80 cotton finished with DMEU

Sample	pH of fabric	Period of aging	Initial strength, warp	Strength after 1 wash* + AATCC 69–1952	Strength after 3 washes* + AATCC 69–1952
Water	6.8	6 mo.	55	53	51
5% DMEU	5.1	1 wk.	36	32	18
5% DMEU	5.1	1 mo.	38	26	14
5% DMEU	5.1	6 mo.	40	15	9
5% DMEU	6.0	1 wk.	38	37	32
5% DMEU	6.0	1 mo.	37	35	24
5% DMEU	6.0	6 mo.	38	21	12
5% DMEU	7.0	6 mo.	36	36	35

* Laundry operation consisted in washing fabric for ½ hr. in soap solution at 160° F. Sample ironed after each wash.

The results indicate that DMEU finishes undergo a slow but progressive degradation during aging when stored under acidic conditions. The degradation may be arrested by alkalinizing the fabric.

TABLE VII. Effect of pH on Development of Damaging Chlorine Retention During Storage (Home Laundering) at 160° F.

Variable—pH
Fabric—80 × 80 cotton finished with DMEU

Sample	pH of fabric	pH adjusting agent	Aging time	Initial strength, warp	Strength after 1 wash* + AATCC 69–1952	Strength after 5 washes* + AATCC 69–1952
Water	—	—	—	54	53	51
5% DMEU	5.1	Monosodium phosphate	1 wk.	37	31	17
5% DMEU	5.1	Monosodium phosphate	6 mo.	39	12	8
5% DMEU	6.0	Mixture of monosodium and disodium phosphate	1 wk.	36	34	18
5% DMEU	6.0	Mixture of monosodium and disodium phosphate	6 mo.	40	16	12
5% DMEU	6.5	Boric acid	1 wk.	38	38	36
5% DMEU	6.5	Boric acid	6 mo.	38	37	29
5% DMEU	7.1	Soda ash rinse	1 wk.	36	37	35
5% DMEU	7.1	Soda ash rinse	6 mo.	35	34	33
5% DMEU	7.8	Disodium phosphate	1 wk.	37	36	36
5% DMEU	7.8	Disodium phosphate	6 mo.	36	35	34

* Laundering operation consisted in washing fabric for ½ hr. in soap solution at 160° F. Fabric washed after each rinse.

The results conform to those recorded in Table VI and indicate that DMEU finishes are hydrolyzed during aging with the development of potentional damaging chlorine-retentive properties. The extent of damage is greater than that resulting from lower temperatures of laundering and less drastic bleaching as shown in Table VIII.

tional bleaching operations and AATCC Method 69–1952.

Influence of Steaming on Chlorine Retentive Properties of Resin Finishes

Mechanical finishing almost always constitutes the final stage of fabric production and is used to remove wrinkles, mask weaving imperfections, stabilize and compress the structure of fabrics, and impart that new feel and look so esteemed by the ultimate consumer. Stretch, tension, temperature, pressure, and steam are the chief elements involved in mechanical finishing. Of these, only steam exerts an appreciable influence on cyclic urea-formaldehyde finishes. The action is drastic, resulting in the unblocking of amide radicals in the finish after only a few seconds of exposure. It is a practice in some mills to expose resin-treated cotton goods after curing and rinsing to a steaming operation and passage of the fabric through a "Sanforized" unit, the object of the operation being to improve the handle and appearance of the cloth. Steaming is also occasionally resorted to in laundering and drycleaning.

Although steaming is not a common cause of damaging chlorine retention in wash-and-wear fabrics, failures traceable to this factor do occur and may be more common than we assume.

We have conducted tests to determine the magnitude of the influence of live steam in rendering an otherwise satisfactory wash-and-wear fabric susceptible to bleach and ironing damage.

Our tests consisted in exposing wash-and-wear cotton goods, that had been finished with DMEU, cured, and rinsed, to live steam for a predetermined period of time. The steamed fabrics were then aged for one week and tested for scorch damage after

TABLE VIII. Effect of pH on Development of Damaging Chlorine Retention During Storage (Mild Laundering)

Variable—pH
Fabric—80 × 80 cotton finished with DMEU

Sample	pH of fabric	pH adjusting agent	Aging time, mo.	Initial strength, warp	Strength after 10 washes* + 0.01% chlorine	Strength after 20 washes* + 0.01% chlorine
Water	—	—	6	56	53	51
5% DMEU	5.1	Monosodium phosphate	6	40	38	29
5% DMEU	6.0	Mixture of monosodium and disodium phosphate	6	38	37	34
5% DMEU	6.5	Boric acid	6	38	36	35
5% DMEU	7.1	Soda ash rinse	6	36	34	33
5% DMEU	7.8	Disodium phosphate	6	37	36	34
5% DMEU	8.2	Tetrasodium pyrophosphate	6	35	34	32

* Laundering occurred with full cycle automatic home laundry machine with synthetic detergent at 120° F.

TABLE IX. Influence of Steaming on Damaging Chlorine Retentive Properties of Resin-Treated Cotton Goods

Fabric—80 × 80 cotton goods

Sample	pH of fabric	Time and temperature of steaming		Initial strength, warp	Strength after 1 wash* + 0.01% chlorine	Strength after 1 wash* + AATCC 69–1952
		Sec.	° F.			
Water	—	0		54	54	55
5% DMEU	7.1	0		39	38	39
5% DMEU	7.1	15	213	38	34	26
5% DMEU	7.1	30	214	36	31	24
5% DMEU	7.1	60	214	37	29	21

* Samples were washed for ½ hr. in 0.25% soap solution at 160° F.

The tests indicate that steaming can be a potent factor in producing an enhanced susceptibility to bleach-scorch damage of fabrics finished with cyclic urea-formaldehyde condensates.

washing, bleaching, and ironing by conventional procedures. The results of the tests are contained in Table IX.

Sunlight is also an important factor in producing the deterioration of textile fibers and most chemical finishes. Tests were arranged to determine the influence of this factor on cyclic urea-formaldehyde finishes, particularly on their tendencies to become chlorine retentive during washing and bleaching.

This study produced some surprising results. The finish did afford some protection of the cotton against degradation, but we were unable to discover any essential changes in the properties of the DMEU finish. The finished cotton goods were no more susceptible to scorch damage after an exposure of six months to atmospheric agencies than materials stored out of contact with light.

Summary

The results of our study on the development of potentially damaging chlorine retention by cyclic urea-formaldehyde finishes and particularly DMEU indicates:

1. Such finishes when affixed onto cotton goods may undergo a change during aging or laundering, with the formation of progenitors of chlorine retention. This change may be minimized, but not entirely prevented, by producing a "tight set" on cotton goods by high concentration of catalyst and elevated curing temperatures. Such a set results in a fabric serviceable under home conditions of laundering, but sensitive to acquiring damaging amounts of chlorine after commercial laundering.

2. The factors that accelerate the formation of chlorine retention precursors are laundering, storage of finished fabrics under adverse conditions (acidic), steaming, and possibly sunlight.

Inhibition of the development of damaging chlorine retention on resin-treated cotton goods can generally be secured by maintaining the fabric neutral or slightly alkaline. Such a precaution is ordinarily sufficient to protect it from damage in all excepting the more vigorous laundering, bleaching, and ironing procedures.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Moisture Regain of Tightly Woven Cotton Fabrics

Southern Regional Research Laboratory [1]
New Orleans 19, Louisiana
October 16, 1958

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In the chemical modification or dyeing of cotton fibers, the velocity and extent of reaction or of dye uptake are favored by a swelling of the cellulose, which permits better penetration of the reactants into the fibers. Such reactions may be slower or less complete if the fibers are restrained from swelling freely. The fibers in a tightly woven fabric are pressed much more closely together than those in an open-weave fabric or in the original yarns, as shown by the pore-size distribution in the interfiber pore-size region [4]. Thus restrained, the fibers are not free to swell, and therefore to imbibe water, to their full capacity.

Preston and Nimkar [3] illustrated this effect by an experiment in which the water retentions of a tightly woven unproofed viscose gabardine and of the yarns dissected therefrom were determined after soaking in water and centrifuging. A 65% moisture retention was found for the fabric and a 75% retention for the yarns. The present experiments were performed to determine whether this effect would be measurable when the fabric and yarns are exposed to water vapor instead of to liquid water.

Two unsized, tightly woven, 10-oz. gray cotton oxfords were used. Both had been woven from 30/2's yarns with 124 warp threads and 72 filling threads to the inch. Fabric A was from mature Deltapine cotton (maturity count 83%) and Fabric B from immature "Sike" cotton (maturity count 30%). These fabrics have been described in detail as samples 118-G and 123-G, respectively, in a previous report [2].

Two approximately 2.5-g. specimens were prepared from Fabric A: a swatch of the fabric and the loose yarns dissected with forceps from a similar swatch. These were placed in tared glass-stoppered weighing bottles and weighed at intervals during successive seven-day periods of exposure to different atmospheric conditions. During the first period they were equilibrated by adsorption under standard textile testing-room conditions, 70° F. and 65% relative humidity. They were then exposed to a high relative humidity by transferring the weighing bottles to a desiccator over an open dish of water and placing in a room kept at approximately 40° F. This temperature was chosen in order to prevent the development of mildew [1]. After seven days, though equilibrium had not been reached, the samples were returned to the textile testing room and equilibrated by desorption. Finally, they were heated to constant weight in an oven at 105–110° C. to obtain their dry weights. These were used to calculate the moisture re-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I. Moisture Regains of Fabric and Yarn Specimens*

Exposure, days‡	Fabric A			Fabric B		
	Fabric %	Yarns %	Δ† %	Fabric %	Yarns %	Δ† %
	Standard conditions (70° F., 65% RH)					
0	5.44	5.74	0.30	5.41	5.81	0.40
1	6.74	7.22	0.48	7.37	7.79	0.42
2	6.82	7.33	0.51	7.55	7.94	0.49
3	—	—	—	7.26	7.73	0.47
4	6.67	7.01	0.34	—	—	—
5	7.03	7.38	0.35	7.39	7.80	0.41
6	6.99	7.35	0.36	7.34	7.60	0.26
7	7.07	7.47	0.40	7.60	7.97	0.37
	40° F., high RH					
8	9.86	9.74	−0.12	10.54	10.70	0.16
9	11.30	11.28	−0.02	12.07	12.69	0.62
10	12.38	12.63	0.25	—	—	—
11	12.88	13.47	0.59	—	—	—
12	13.58	14.46	0.88	15.49	16.44	0.95
13	—	—	—	15.85	17.13	1.28
14	14.34	15.67	1.33	16.09	17.68	1.59
	Standard conditions (70° F., 65% RH)					
15	8.74	9.16	0.42	9.26	9.57	0.31
16	8.88	9.10	0.22	9.38	9.81	0.43
17	8.70	8.94	0.24	—	—	—
18	8.68	9.00	0.32	—	—	—
19	—	—	—	9.33	9.51	0.18
20	—	—	—	9.35	9.57	0.22
21	8.71	9.00	0.29	—	—	—

* Although the moisture regains are given to the nearest 0.01% as determined, this degree of accuracy is not claimed.
† Moisture regain of yarns minus that of fabric specimen.
‡ Cumulative.

gains at the various stages of the experiment. The process was then repeated with corresponding specimens from Fabric B.

The results are given in Table I, which includes the values for Δ, the percent moisture regain of the loose yarns minus that for the fabric specimen. Under standard conditions Δ ranged from + 0.22 to + 0.51%, showing that the moisture sorption of the yarn was consistently greater than that of the fabric whether the approach to equilibrium was by adsorption or by desorption, though the regains by adsorption were, of course, lower than by desorption. The fact that the moisture regains of the immature cotton samples were consistently higher than those of the mature samples under the same conditions can perhaps be attributed to a difference in the nature or proportion of the noncellulosic constituents in the two cottons or to some factor dependent upon the difference in weight fineness and cross-sectional shape of the fibers.

Equilibrium was approached much more slowly during the exposure to the high relative humidity, since the air in the desiccator was not in motion. Therefore, as would be expected from the relative bulk volumes, and consequently the accessibilities, of the sample materials, the initial rate of increase of the moisture regain for the yarn samples during this period was lower than that for the fabric specimens. This explains the negative values of Δ for Fabric A for the eighth and ninth days. Though equilibrium had still not been reached at the end of the fourteenth day, the values of Δ for Fabrics A and B had increased to + 1.33 and + 1.59, respectively.

It can be concluded that the mechanical restraints to swelling in a tightly woven cotton fabric are sufficient to result in a measurably lower moisture regain than that for the loose yarns when exposed to even moderate relative humidities. The compression of the fibers prevents them from swelling freely and thus limits the amount of water they can sorb.

That stresses were developed in the fabric specimens was shown by the fact that at high moisture contents the yarns at the edges were pushed loose from the body of the swatches. This indicates that under the condition of these experiments the stresses were relieved to a certain extent. If this had been prevented (if, for example, the measurements had been made on a very large fabric specimen), the differences between the moisture regain of the fabric and the loose yarns at the high relative humidity would undoubtedly have been even greater.

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Book Review

Flow of Gases Through Porous Media. P. C. Carman. New York, Academic Press, 1956. ix + 182 pages, illust. Price $6.00.

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In this relatively small book, the author has given a comprehensive and quantitative discussion of the flow of gases through porous media. To limit the size of the book, upper and lower limits have been placed on the degree of porosity of the solid. Packed columns, in which the analysis of the flow is essentially a problem in turbulent fluid dynamics, have been excluded from consideration. So also have solids with pores of molecular dimensions, although many of the concepts applicable in this case have been introduced in connection with discussions of surface diffusion. As a result of this emphasis, the Kozeny-Carman equation for flow in unconsolidated media with random pore structure plays a central part. Much attention is given to the limitations and utility of this equation and to suitable alterations which can be introduced to account for changes in pore texture, Knudsen flow, or the flow of sorbable gases. In addition to the general discussion of flow, chapters on the separation of gas mixtures and the permeability method of surface area measurement are included. Problems involving liquids are discussed only incidentally.

The author has done workers in the field a service by gathering together a considerable amount of information from widely scattered sources and presenting it in a logical manner. Emphasis is placed on quantitative theoretical development insofar as possible; however, since derivations of equations are sometimes rather sketchy, the book will be of more use to research workers in the field than to novices and students.

The book will make a valuable addition to any comprehensive library on textile materials, not only because many problems of technical importance in the textile field fall within its scope, but also because much work on fibers is included in it.